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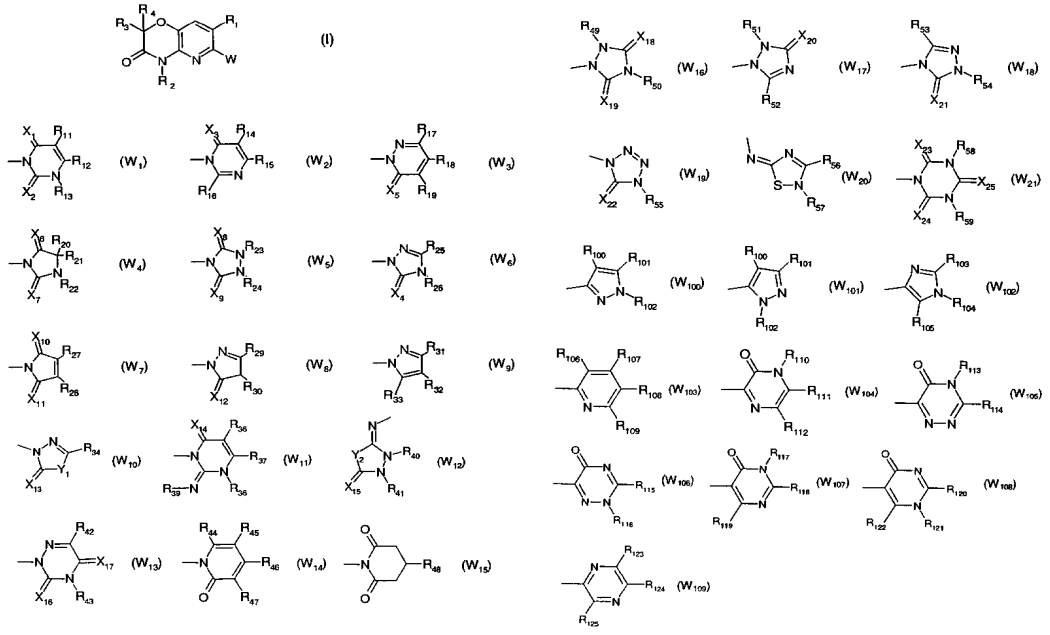
(54) **Title:** NOVEL HERBICIDES



(57) **Abstract:** Compounds of formula (I) wherein R_1-R_4 and W are as defined in the description and the agrochemically acceptable salts and tautomers, enantiomers and stereoisomers of such compounds of formula (I), are suitable for use as herbicides.

WO 01/30782 A2

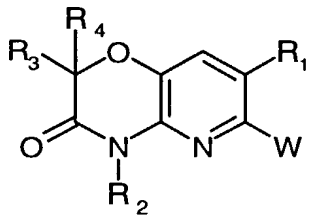
Novel herbicides

The present invention relates to novel, herbicidally active 4H-pyrido[3,2-b][1,4]oxazin-3-ones substituted by nitrogen heterocycles, to processes for the preparation thereof, to compositions comprising those compounds, and to the use thereof in the control of weeds, especially in crops of useful plants, for example cereals, maize, rice, cotton, soybeans, rape, sorghum, sugar cane, sugar beet, sunflowers, vegetables, plantation crops and fodder plants, or in the inhibition of plant growth, and also in the non-selective control of weeds.

N-Pyridyl-imides, N-pyridyl-pyrazoles and N-pyridyl-triazolidinones and also N-pyridyl-uracils and N-pyridonyl-uracils having herbicidal activity are described, for example, in DE 3 917 469, WO 98/27082, WO 98/27083, WO 98/52938, WO 98/42698, WO 98/21199, WO 99/52892 and WO 99/52893.

Novel heterocyclic derivatives of 6-amino-4H-pyrido[3,2-b][1,4]oxazin-3-one and 3-oxo-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazine-6-carboxylic acid which are substituted in the 6-position and have herbicidal and growth-inhibiting properties have now been found.

The present invention accordingly relates to compounds of formula I



(I) ,

wherein

R_1 is hydrogen, methyl or halogen;

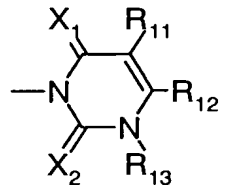
R_2 is hydrogen, C_1-C_{12}alkyl, C_1-C_{12}haloalkyl, C_2-C_{12}alkenyl, C_2-C_{12}alkynyl, C_2-C_8alkynyl-C_2-C_4alkenyl, C_3-C_{12}allenyl, C_2-C_{12}haloalkenyl, C_2-C_{12}haloalkynyl, C_3-C_6cycloalkyl, C_3-C_6cycloalkyl-C_1-C_4alkyl, C_3-C_6halocycloalkyl-C_1-C_4alkyl, tri(C_1-C_4alkyl)silyl-C_1-C_4alkyl, tri(C_1-C_4alkyl)silyl-C_2-C_4alkenyl, cyano-C_1-C_{12}alkyl, C_1-C_6alkoxy-C_1-C_4alkyl, C_1-C_4alkoxy-C_1- or -C_2-alkoxy-C_1- or -C_2-alkyl, di(C_1-C_4alkoxy)-C_1- or -C_2-alkyl, ethylenedioxy-C_1- or -C_2-alkyl, C_2-C_6alkenyloxy-C_1-C_4alkyl, C_2-C_6haloalkenyloxy-C_1-C_4alkyl, C_2-C_6alkynyloxy-C_1-C_4alkyl, C_3-C_6haloalkynyloxy-C_1-C_4alkyl, C_1-C_6alkylthio-C_1-C_4alkyl, C_1-C_6alkylsulfinyl-C_1-C_4alkyl, C_1-

C_6alkylsulfonyl-C_1-C_4alkyl, hydroxy-C_1-C_{12}alkyl, C_1-C_6alkylcarbonyl-C_1-C_4alkyl, C_1-C_6haloalkylcarbonyl-C_1-C_4alkyl, C_1-C_6alkoxycarbonyl-C_1-C_4alkyl, C_1-C_6alkoxy-C_1- or -C_2-alkoxycarbonyl-C_1-C_4alkyl, C_1-C_6alkoxycarbonyl-C_1-C_4haloalkyl, C_3-C_6cycloalkylcarbonyl-C_1-C_4alkyl or benzoyl-C_1-C_4alkyl wherein the benzoyl group may be substituted by halogen, C_1-C_3alkyl, C_1-C_3haloalkyl, C_1-C_3alkoxy or by C_1-C_3haloalkoxy, or is C_3-C_6alkenyloxycarbonyl-C_1-C_4alkyl, C_3-C_6alkynyloxycarbonyl-C_1-C_4alkyl, C_1-C_6alkylcarbonyloxy-C_1-C_4alkyl, C_2-C_6alkenylcarbonyloxy-C_1-C_4alkyl, C_3-C_6cycloalkylcarbonyloxy-C_1-C_4alkyl, benzoyloxy-C_1-C_4alkyl, C_1-C_6alkoxycarbonyloxy-C_1-C_4alkyl, carbamoyl-C_1-C_4alkyl, C_1-C_6alkylaminocarbonyl-C_1-C_4alkyl, or phenyl- or heterocyclyl-substituted C_1-C_4alkyl wherein the phenyl and heterocyclyl groups may be substituted by halogen, C_1-C_6alkyl, C_1-C_6alkoxy, C_1-C_6haloalkyl, C_1-C_6haloalkoxy, C_2-C_6alkenyl, C_2-C_6alkynyl, C_2-C_6haloalkenyl, C_2-C_6haloalkynyl, C_3-C_6cycloalkyl-C_1-C_4alkyl, C_3-C_6halocycloalkyl-C_1-C_4alkyl, cyano-C_1-C_4alkyl, C_1-C_6alkoxy-C_1-C_4alkyl, C_1-C_6alkylthio-C_1-C_4alkyl, C_1-C_6alkylsulfinyl-C_1-C_4alkyl, C_1-C_6alkylsulfonyl-C_1-C_4alkyl, hydroxy-C_1-C_4alkyl, C_1-C_6alkylcarbonyl-C_1-C_4alkyl, C_1-C_6alkoxycarbonyl, C_1-C_6alkoxy-carbonyl-C_1-C_4alkyl, C_1-C_6alkoxycarbonyl-C_1-C_4haloalkyl, C_1-C_6alkoxycarbonyl-C_1-C_4alkoxy, C_1-C_6alkylcarbonyloxy-C_1-C_4alkyl, C_1-C_6alkoxycarbonyloxy-C_1-C_4alkyl, C_1-C_4alkoxy-C_1-C_2alkoxy-C_1-C_2alkyl, C_1-C_4alkylaminocarbonyl, C_1-C_6alkylaminocarbonyl-C_1-C_4alkoxy, phenyl, phenoxy or by benzyloxy, wherein the phenyl ring of the last three definitions may be substituted by halogen, methyl, trifluoromethyl, methylsulfonyl, methoxy, ethoxy or by cyano; or is phenyl-substituted C_2-C_4alkenyl or C_2-C_4alkynyl, wherein the phenyl group may be substituted by halogen, methyl, trifluoromethyl, methylthio, methylsulfinyl, methylsulfonyl, methoxy, ethoxy, cyano or by nitro;

R_3 is hydrogen, C_1-C_{12}alkyl, C_1-C_{12}haloalkyl, C_1-C_6alkoxycarbonyl, or phenyl which is unsubstituted or substituted by halogen, methyl, trifluoromethyl, methylthio, methylsulfinyl, methylsulfonyl, methoxy, ethoxy, cyano or by nitro;

R_4 is hydrogen or C_1-C_6alkyl;

W is a group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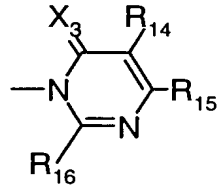
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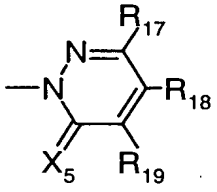
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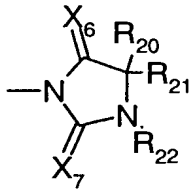
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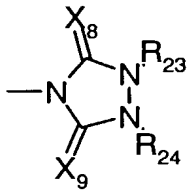
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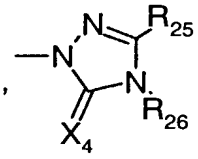
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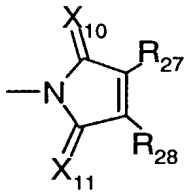
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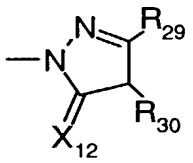
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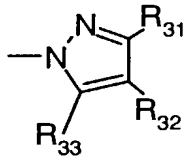
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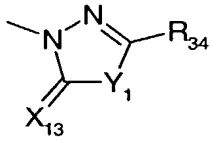
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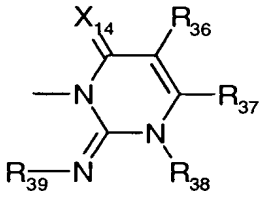
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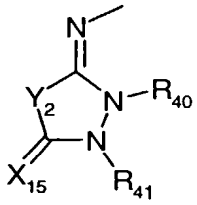
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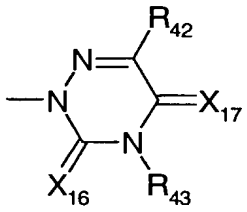
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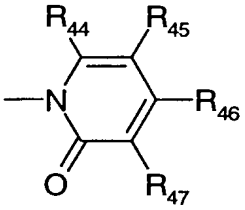
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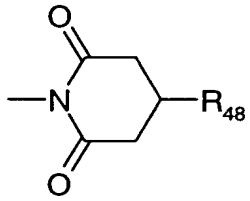
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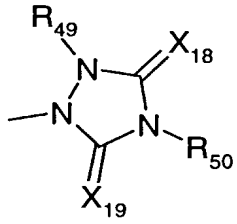
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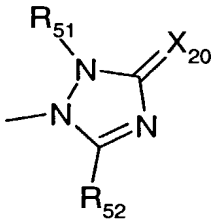
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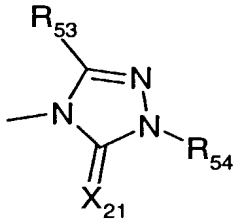
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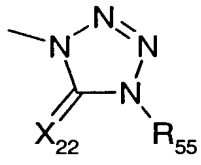
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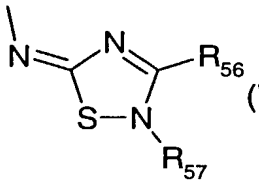
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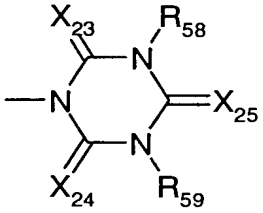
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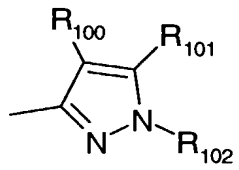
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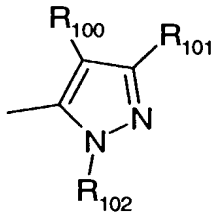
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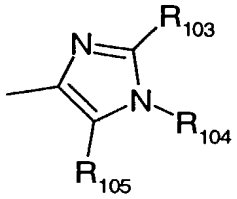
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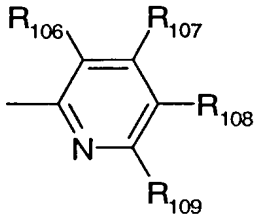
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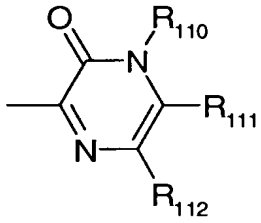
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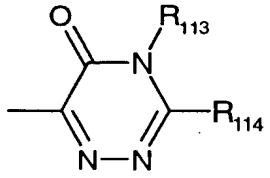
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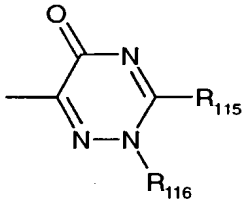
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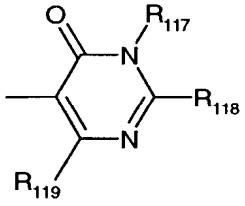
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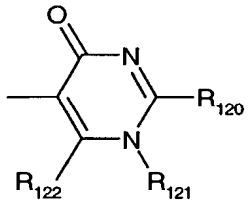
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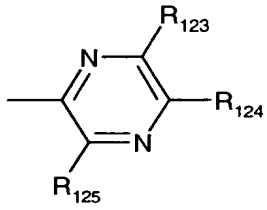

(W_{109});

R_{11} is hydrogen, C_1-C_3alkyl, halogen, C_1-C_3haloalkyl or cyano;

R_{12} is C_1-C_3alkyl, C_1-C_3haloalkyl, C_1-C_3alkyl-S(O)$_{n1}$-, C_1-C_3haloalkyl-S(O)$_{n1}$- or cyano; and

R_{13} is hydrogen, C_1-C_3alkyl, C_1-C_3haloalkyl, allyl, propargyl or amino; or

R_{12} and R_{11} or R_{12} and R_{13} together form a C_3- or C_4-alkylene bridge which may be substituted by halogen, C_1-C_3haloalkyl or by cyano;

R_{14} is hydrogen, C_1-C_3alkyl, halogen, C_1-C_3haloalkyl or cyano; and

R_{15} is C_1-C_3alkyl, C_1-C_3haloalkyl, C_1-C_3alkyl-S(O)$_{n2}$-, C_1-C_3haloalkyl-S(O)$_{n2}$- or cyano; or

R_{15} and R_{14} together form a C_3- or C_4-alkylene bridge which may be substituted by halogen, C_1-C_3haloalkyl or by cyano;

R_{16} is hydrogen, C_1-C_3alkyl, halogen, C_1-C_3haloalkyl, C_1-C_3alkoxy, C_1-C_3haloalkoxy, hydroxy, mercapto, C_1-C_3alkylthio, C_1-C_3alkylsulfinyl, C_1-C_3alkylsulfonyl, allylthio, propargylthio, amino, C_1-C_3alkylamino, di(C_1-C_3alkyl)amino, allylamino, propargylamino or cyano;

n_1 and n_2 are 0, 1 or 2;

R_{17} is hydrogen, C_1-C_3alkyl, halogen or cyano; and

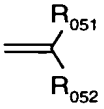
R_{18} is C_1-C_3alkyl, halogen, C_1-C_3haloalkyl, C_1-C_3alkylthio, C_1-C_3alkylsulfinyl, C_1-C_3alkylsulfonyl or cyano; or

R_{18} and R_{17} together form a C_3- or C_4-alkylene or C_3- or C_4-alkenylene bridge, both of which may be substituted by halogen, C_1-C_3alkyl or by C_1-C_3haloalkyl;

R_{19} is hydrogen, halogen, C_1-C_3alkyl, carboxyl, C_1-C_3alkoxycarbonyl or amino; or

R_{19} and R_{18} together form a C_3- or C_4-alkylene or C_3- or C_4-alkenylene bridge, both of which may be substituted by halogen, C_1-C_3alkyl or by C_1-C_3haloalkyl;

R_{20} and R_{21} are each independently of the other hydrogen or C_1-C_4alkyl; or

R_{20} and R_{21} together are a group  ;

R_{051} and R_{052} are each independently of the other hydrogen or C_1-C_4alkyl; or

R_{051} and R_{052} together form a C_4- or C_5-alkylene bridge;

R_{052} and R_{22} together form a C_3alkylene bridge;

R_{22} is hydrogen or C_1-C_3alkyl; or

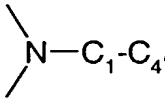
R_{22} and R_{20} or R_{22} and R_{21} together form a C_3-C_5alkylene bridge which may be interrupted by oxygen, sulfur, -S(O)-, -$S(O)_2$- or by -C(O)- and/or substituted by halogen, C_1-C_4alkyl, C_1-C_3haloalkyl, C_2-C_4alkenyl, C_1-C_3alkoxycarbonyl, C_1-C_3alkylcarbonyloxy, C_1-C_3alkylsulfonyloxy or by hydroxy;

R_{23} and R_{24} are each independently of the other hydrogen, C_1-C_3alkyl, C_1-C_3haloalkyl or propargyl; or

R_{23} and R_{24} together form a C_3-C_5alkylene bridge which may be interrupted by oxygen, sulfur, -S(O)-, -$S(O)_2$- or by -C(O)- and/or substituted by halogen, C_1-C_4alkyl, hydroxy, C_1-C_4alkoxy or by C_1-C_4alkoxy-C_1-C_4alkoxy;

R_{25} is hydrogen, halogen, C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4alkoxy, C_1-C_4haloalkoxy, C_1-C_4alkylthio, C_1-C_4haloalkylthio, C_1-C_4alkylsulfinyl, C_1-C_4haloalkylsulfinyl, C_1-C_4alkylsulfonyl, C_1-C_4haloalkylsulfonyl, hydroxy or cyano; and

R_{26} is hydrogen, C_1-C_4alkyl or C_1-C_4haloalkyl; or

R_{26} and R_{25} together form a C_3-C_5alkylene bridge which may be interrupted by oxygen, sulfur, -S(O)-, -$S(O)_2$-,  or by -C(O)- and/or substituted by halogen, C_1-C_4alkyl, C_1-C_3haloalkyl, C_2-C_4alkenyl, C_1-C_3alkoxycarbonyl, C_1-C_3alkylcarbonyloxy, C_1-C_3alkylsulfonyloxy or by hydroxy;

R_{27} and R_{28} are each independently of the other hydrogen or C_1-C_4alkyl; or
R_{27} and R_{28} together form a C_3-C_5alkylene bridge which may be substituted by halogen or by C_1-C_4alkyl and/or interrupted by oxygen, sulfur, -S(O)-, -$S(O)_2$- or by -C(O)- or form a C_4alkenylene bridge which is unsubstituted or substituted by C_1-C_4alkyl;
R_{29} and R_{30} are each independently of the other hydrogen, C_1-C_4alkyl or C_1-C_4haloalkyl; or
R_{29} and R_{30} together form a C_3-C_5alkylene bridge which may be substituted by halogen or by C_1-C_4alkyl and/or interrupted by oxygen, sulfur, -S(O)-, -$S(O)_2$- or by -C(O)-;
R_{31} is hydrogen, C_1-C_4alkyl or C_1-C_4haloalkyl; and
R_{32} is hydrogen, C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4alkylthio, C_1-C_4alkylsulfinyl, C_1-C_4alkylsulfonyl, cyano or nitro; or
R_{31} and R_{32} together form a C_3-C_5alkylene bridge which may be substituted by halogen or by C_1-C_4alkyl and/or interrupted by oxygen, sulfur, -S(O)-, -$S(O)_2$- or by -C(O)- or form a C_4alkenylene bridge which is unsubstituted or substituted by C_1-C_4alkyl;
R_{33} is hydrogen, C_1-C_3alkyl, halogen, C_1-C_3haloalkyl, hydroxy, C_1-C_3alkoxy, C_1-C_3haloalkoxy, mercapto, C_1-C_3alkylthio, C_1-C_3alkylsulfinyl, C_1-C_3alkylsulfonyl, amino, C_1-C_3alkylamino, C_1-C_3alkylcarbonylamino, C_1-C_3haloalkylcarbonylamino or cyano;
R_{34} is C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4alkoxy or C_1-C_4alkylthio;
R_{36} is hydrogen, C_1-C_3alkyl, halogen, C_1-C_3haloalkyl or cyano; and
R_{37} is C_1-C_3alkyl, C_1-C_3haloalkyl, C_1-C_3alkyl-$S(O)_{n1}$-, C_1-C_3haloalkyl-$S(O)_{n1}$- or cyano; or
R_{37} and R_{36} together form a C_3- or C_4-alkenylene bridge which may be substituted by halogen, C_1-C_3alkyl, C_1-C_3haloalkyl or by cyano;
R_{38} is C_1-C_3alkyl; and
R_{39} is hydrogen or C_1-C_3alkyl; or
R_{39} and R_{38} together form a C_2- or C_3-alkylene or C_2- or C_3-alkenylene bridge which is unsubstituted or substituted by C_1-C_4alkyl or form an -NH-CH_2-, -N=CH- or -N=N- bridge;
R_{40} and R_{41} are each independently of the other C_1-C_3alkyl or C_1-C_3haloalkyl; or
R_{41} and R_{40} together form a C_3-C_5alkylene bridge which is unsubstituted or substituted by halogen or by C_1-C_4alkyl;
R_{42} is hydrogen, C_1-C_3alkyl, C_1-C_3haloalkyl, cyano or carboxyl;
R_{43} is hydrogen, C_1-C_3alkyl, C_1-C_3haloalkyl, allyl or propargyl;
R_{44} is hydrogen, C_1-C_3alkyl, halogen, C_1-C_3haloalkyl, hydroxy, mercapto, amino, C_1-C_3alkoxy, C_1-C_3alkylthio or di(C_1-C_4alkyl)amino;
R_{45} is hydrogen, C_1-C_3alkyl, halogen or cyano;
R_{46} is C_1-C_3alkyl, C_1-C_3haloalkyl or cyano;
R_{47} is hydrogen, C_1-C_3alkyl or halogen;

R_{48} is C_1-C_3alkyl or C_1-C_3haloalkyl;

R_{49}, R_{50} and R_{51} are each independently of the others hydrogen, C_1-C_4alkyl, propargyl or C_1-C_4haloalkyl;

R_{52} is C_1-C_3alkyl, halogen, C_1-C_3haloalkyl, C_1-C_3alkoxy, C_1-C_3haloalkoxy, C_1-C_3alkylthio, C_1-C_3alkylsulfinyl, C_1-C_3alkylsulfonyl, amino or C_1-C_3alkylamino;

R_{53} is C_1-C_3alkyl or C_1-C_3haloalkyl;

R_{54} is C_1-C_3alkyl;

R_{55} is hydrogen, C_1-C_3alkyl, propargyl or C_1-C_3haloalkyl;

R_{56} is C_1-C_3alkyl, C_1-C_3haloalkyl, C_1-C_3alkylthio, C_1-C_3alkylsulfinyl or C_1-C_3alkylsulfonyl; and

R_{57} is C_1-C_3alkyl or C_1-C_3haloalkyl; or

R_{57} and R_{56} together form a C_2-C_4alkylene or C_2-C_4alkenylene bridge which both are unsubstituted or substituted by halogen or by C_1-C_4alkyl;

R_{58} is hydrogen, C_1-C_3alkyl, C_1-C_3haloalkyl or amino;

R_{59} is hydrogen, C_1-C_3alkyl or C_1-C_3haloalkyl;

R_{100} is hydrogen, halogen, nitro, amino, cyano, C_1-C_3alkyl, C_2- or C_3-alkenyl or C_2- or C_3-alkynyl;

R_{101} is hydrogen, halogen, nitro, amino, cyano, hydroxy, mercapto, C_1-C_3alkyl, C_1-C_3haloalkyl, C_2- or C_3-alkenyl, C_2- or C_3-alkynyl, C_1-C_3alkoxy, C_1-C_3haloalkoxy, C_1-C_3alkylthio, C_1-C_3alkylsulfinyl, C_1-C_3alkylsulfonyl, C_1-C_3haloalkylthio, C_1-C_3haloalkylsulfinyl, C_1-C_3haloalkylsulfonyl, $FS(O)_2$-, $ClS(O)_2$-, C_1-C_6alkylsulfonyloxy, C_1-C_6haloalkylsulfonyloxy, C_1-C_3alkylcarbonyl, HC(O)-, HOC(O)-, ClC(O)-, FC(O)-, C_1-C_3alkoxycarbonyl, $H_2NC(O)$- or $H_2NC(S)$-; and

R_{102} is hydrogen, C_1-C_6alkyl, C_1-C_6alkyl substituted by cyano, HO-, HOC(O)-, C_1-C_3alkoxycarbonyl or by HC(O)-, or is C_3-C_6alkenyl, C_3-C_6alkynyl, C_3-C_6cycloalkyl, C_1-C_6haloalkyl or C_1-C_3alkylsulfonyl; or

when W is a group W_{100},

R_{102} and R_{101} together form a C_3-C_5alkylene bridge which may be interrupted by oxygen, sulfur, -S(O)-, $-S(O)_2$- or by -C(O)- and/or substituted by hydroxy or by halogen;

R_{103} is hydrogen, halogen, nitro, amino, cyano, hydroxy, mercapto, C_1-C_3alkyl, C_1-C_3haloalkyl, C_2- or C_3-alkenyl, C_2- or C_3-alkynyl, C_1-C_3alkoxy, C_1-C_3haloalkoxy, C_1-C_3alkylthio, C_1-C_3alkylsulfinyl, C_1-C_3alkylsulfonyl, C_1-C_3haloalkylthio, C_1-C_3haloalkylsulfinyl, C_1-C_3haloalkylsulfonyl, $FS(O)_2$-, $ClS(O)_2$-, C_1-C_6alkylsulfonyloxy, C_1-C_6haloalkylsulfonyloxy, C_1-C_3alkylcarbonyl, HC(O)-, HOC(O)-, ClC(O)-, FC(O)-, C_1-C_3alkoxycarbonyl, $H_2NC(O)$- or $H_2NC(S)$-;

R_{104} is hydrogen, C_1-C_6alkyl, C_1-C_6alkyl substituted by cyano, HO-, HOC(O)-, C_1-C_3alkoxy-carbonyl or by HC(O)-, or is C_3-C_6alkenyl, C_3-C_6alkynyl, C_3-C_6cycloalkyl, C_1-C_6haloalkyl or C_1-C_3alkylsulfonyl; and

R_{105} is hydrogen, halogen, nitro, amino, cyano, C_1-C_3alkyl, C_2- or C_3-alkenyl or C_2- or C_3-alkynyl; or

R_{104} and R_{103} together form a C_3-C_5alkylene bridge or a C_4alkenylene bridge which both may be interrupted by oxygen, sulfur, -S(O)-, -$S(O)_2$- or by -C(O)- and/or substituted by hydroxy or by halogen;

R_{106} is hydrogen, halogen, amino, nitro, hydroxy, C_1-C_3alkyl or C_1-C_3alkoxy;

R_{107} is hydrogen, halogen, amino, hydroxy, C_1-C_3alkyl, C_1-C_3haloalkyl, HC(O)-, HOC(O)-, hydroxy-C_1-C_3alkyl, C_1-C_3alkoxy or C_1-C_3haloalkoxy; and

R_{108} is hydrogen, halogen, nitro, amino, cyano, HC(O)-, HOC(O)-, $H_2NC(O)$-, $H_2NC(S)$-, hydroxy, mercapto, C_1-C_3alkyl, C_1-C_3haloalkyl, C_2- or C_3-alkenyl, C_1-C_3alkoxy, C_1-C_3haloalkoxy, C_1-C_3alkylcarbonyl, C_1-C_3alkoxycarbonyl, C_1-C_3alkylthio, C_1-C_3haloalkylthio, C_1-C_3alkylsulfinyl, C_1-C_3haloalkylsulfinyl, C_1-C_3alkylsulfonyl, C_1-C_3haloalkylsulfonyl, C_1-C_3alkylsulfonyloxy or C_1-C_3haloalkylsulfonyloxy; or

R_{108} and R_{107} together form a C_3-C_5alkylene bridge which may be interrupted by oxygen, sulfur, -S(O)-, -$S(O)_2$- or by -C(O)- and/or substituted by hydroxy or by halogen;

R_{109} is hydrogen, halogen, amino, hydroxy, C_1-C_3alkyl, C_1-C_3haloalkyl, HC(O)-, HOC(O)-, hydroxy-C_1-C_3alkyl, C_1-C_3alkoxy or C_1-C_3haloalkoxy; or

R_{109} and R_{108} together form a C_3-C_5alkylene bridge which may be interrupted by oxygen, sulfur, -S(O)-, -$S(O)_2$- or by -C(O)- and/or substituted by hydroxy or by halogen;

R_{110} is hydrogen, C_1-C_3alkyl, C_1-C_3haloalkyl, C_3-C_4alkenyl or C_3-C_4alkynyl;

R_{111} is hydrogen, halogen, nitro, amino, cyano, HC(O)-, HOC(O)-, $H_2NC(O)$-, $H_2NC(S)$-, hydroxy, mercapto, C_1-C_3alkyl, C_1-C_3haloalkyl, C_2- or C_3-alkenyl, C_1-C_3alkoxy, C_1-C_3haloalkoxy, C_1-C_3alkylcarbonyl, C_1-C_3alkoxycarbonyl, C_1-C_3alkylthio, C_1-C_3haloalkylthio, C_1-C_3alkylsulfinyl, C_1-C_3haloalkylsulfinyl, C_1-C_3alkylsulfonyl, C_1-C_3haloalkylsulfonyl, C_1-C_3alkylsulfonyloxy or C_1-C_3haloalkylsulfonyloxy; and

R_{112} is hydrogen, halogen, amino, hydroxy, C_1-C_3alkyl, C_1-C_3haloalkyl, HC(O)-, HOC(O)-, hydroxy-C_1-C_3alkyl, C_1-C_3alkoxy or C_1-C_3haloalkoxy; or

R_{111} and R_{110} together form a C_3-C_5alkylene bridge which may be interrupted by oxygen, sulfur, -S(O)-, -$S(O)_2$- or by -C(O)- and/or substituted by hydroxy or by halogen, wherein the C_3-C_5alkylene bridge is bonded to the N atom of the pyrazinone *via* a CH_2 group; or

R_{112} and R_{111} together form a C_3-C_5alkylene bridge which may be interrupted by oxygen, sulfur, -S(O)-, -$S(O)_2$- or by -C(O)- and/or substituted by hydroxy or by halogen;

R_{113} is hydrogen, C_1-C_3alkyl, C_1-C_3haloalkyl, C_3-C_4alkenyl or C_3-C_4alkynyl; and

R_{114} is hydrogen, halogen, nitro, amino, cyano, HC(O)-, HOC(O)-, $H_2NC(O)$-, $H_2NC(S)$-, hydroxy, mercapto, C_1-C_3alkyl, C_1-C_3haloalkyl, C_2- or C_3-alkenyl, C_1-C_3alkoxy, C_1-C_3haloalkoxy, C_1-C_3alkylcarbonyl, C_1-C_3alkoxycarbonyl, C_1-C_3alkylthio, C_1-C_3haloalkylthio, C_1-C_3alkylsulfinyl, C_1-C_3haloalkylsulfinyl, C_1-C_3alkylsulfonyl, C_1-C_3haloalkylsulfonyl, C_1-C_3alkylsulfonyloxy, C_1-C_3haloalkylsulfonyloxy, C_1-C_3alkylamino or di(C_1-C_3alkyl)amino; or

R_{114} and R_{113} together form a C_3-C_5alkylene bridge which may be interrupted by oxygen, sulfur, -S(O)-, $-S(O)_2$- or by -C(O)- and/or substituted by hydroxy or by halogen, wherein the C_3-C_5alkylene bridge is bonded to the N atom of the triazinone *via* a CH_2 group;

R_{115} is hydrogen, halogen, nitro, amino, cyano, HC(O)-, HOC(O)-, $H_2NC(O)$-, $H_2NC(S)$-, hydroxy, mercapto, C_1-C_3alkyl, C_1-C_3haloalkyl, C_2- or C_3-alkenyl, C_1-C_3alkoxy, C_1-C_3haloalkoxy, C_1-C_3alkylcarbonyl, C_1-C_3alkoxycarbonyl, C_1-C_3alkylthio, C_1-C_3haloalkylthio, C_1-C_3alkylsulfinyl, C_1-C_3haloalkylsulfinyl, C_1-C_3alkylsulfonyl, C_1-C_3haloalkylsulfonyl, C_1-C_3alkylsulfonyloxy or C_1-C_3haloalkylsulfonyloxy; and

R_{116} is hydrogen, C_1-C_3alkyl, C_1-C_3haloalkyl, C_3-C_4alkenyl or C_3-C_4alkynyl; or

R_{116} and R_{115} together form a C_3-C_5alkylene bridge which may be interrupted by oxygen, sulfur, -S(O)-, $-S(O)_2$- or by -C(O)- and/or substituted by hydroxy or by halogen, wherein the C_3-C_5alkylene bridge is bonded to the N atom of the triazinone *via* a CH_2 group;

R_{117} is hydrogen, C_1-C_3alkyl, C_1-C_3haloalkyl, C_3-C_4alkenyl or C_3-C_4alkynyl;

R_{118} is hydrogen, halogen, nitro, amino, cyano, HC(O)-, HOC(O)-, $H_2NC(O)$-, $H_2NC(S)$-, hydroxy, mercapto, C_1-C_3alkyl, C_1-C_3haloalkyl, C_2- or C_3-alkenyl, C_1-C_3alkoxy, C_1-C_3haloalkoxy, C_1-C_3alkylcarbonyl, C_1-C_3alkoxycarbonyl, C_1-C_3alkylthio, C_1-C_3haloalkylthio, C_1-C_3alkylsulfinyl, C_1-C_3haloalkylsulfinyl, C_1-C_3alkylsulfonyl, C_1-C_3haloalkylsulfonyl, C_1-C_3alkylsulfonyloxy or C_1-C_3haloalkylsulfonyloxy; and

R_{119} is hydrogen, halogen, amino, nitro, hydroxy, C_1-C_3alkyl or C_1-C_3alkoxy; or

R_{118} and R_{117} together form a C_3-C_5alkylene bridge which may be interrupted by oxygen, sulfur, -S(O)-, $-S(O)_2$- or by -C(O)- and/or substituted by hydroxy or by halogen, wherein the C_3-C_5alkylene bridge is bonded to the N atom of the pyrimidinone *via* a CH_2 group;

R_{120} is hydrogen, halogen, nitro, amino, cyano, HC(O)-, HOC(O)-, $H_2NC(O)$-, $H_2NC(S)$-, hydroxy, mercapto, C_1-C_3alkyl, C_1-C_3haloalkyl, C_2- or C_3-alkenyl, C_1-C_3alkoxy, C_1-C_3haloalkoxy, C_1-C_3alkylcarbonyl, C_1-C_3alkoxycarbonyl, C_1-C_3alkylthio, C_1-C_3haloalkylthio, C_1-C_3alkylsulfinyl, C_1-C_3haloalkylsulfinyl, C_1-C_3alkylsulfonyl, C_1-C_3haloalkylsulfonyl, C_1-C_3alkylsulfonyloxy or C_1-C_3haloalkylsulfonyloxy;

R_{121} is hydrogen, C_1-C_3alkyl, C_1-C_3haloalkyl, C_3- or C_4-alkenyl or C_3- or C_4-alkynyl; and

R_{122} is hydrogen, halogen, amino, nitro, hydroxy, C_1-C_3alkyl or C_1-C_3alkoxy; or

R_{121} and R_{120} together form a C_3-C_5alkylene bridge which may be interrupted by oxygen, sulfur, -S(O)-, -$S(O)_2$- or by -C(O)- and/or substituted by hydroxy or by halogen, wherein the C_3-C_5alkylene bridge is bonded to the N atom of the pyrimidinone *via* a CH_2 group;

R_{123} is hydrogen, C_1-C_3alkyl, halogen or C_1-C_3haloalkyl;

R_{124} is hydrogen, halogen, nitro, amino, cyano, HC(O)-, HOC(O)-, $H_2NC(O)$-, $H_2NC(S)$-, hydroxy, mercapto, C_1-C_3alkyl, C_1-C_3haloalkyl, C_2- or C_3-alkenyl, C_1-C_3alkoxy, C_1-C_3haloalkoxy, C_1-C_3alkylcarbonyl, C_1-C_3alkoxycarbonyl, C_1-C_3alkylthio, C_1-C_3haloalkylthio, C_1-C_3alkylsulfinyl, C_1-C_3haloalkylsulfinyl, C_1-C_3alkylsulfonyl, C_1-C_3haloalkylsulfonyl, C_1-C_3alkylsulfonyloxy or C_1-C_3haloalkylsulfonyloxy; and

R_{125} is hydrogen, C_1-C_3alkyl, halogen, hydroxy, C_1-C_3alkoxy, C_1-C_3haloalkoxy, C_1-C_3alkylthio, C_1-C_3alkylsulfinyl, C_1-C_3alkylsulfonyl, amino or cyano;

X_1, X_2, X_3, X_4, X_5, X_6, X_7, X_8, X_9, X_{10}, X_{11}, X_{12}, X_{13}, X_{14}, X_{15}, X_{16}, X_{17}, X_{18}, X_{19}, X_{20}, X_{21}, X_{22}, X_{23}, X_{24} and X_{25} are each independently of the others oxygen or sulfur; and

Y_1 and Y_2 are oxygen or sulfur,

and also the agrochemically acceptable salts and tautomers, enantiomers and stereoisomers of the compounds of formula I.

In the above definitions, halogen is to be understood as being iodine and also, preferably, fluorine, chlorine or bromine.

The alkyl, alkenyl and alkynyl groups appearing in the substituent definitions may be straight-chained or branched, that especially also being true of the alkyl, alkenyl and alkynyl moiety of alkylcarbonyl, alkylcarbonyloxy, alkoxycarbonyl, alkenyloxycarbonyl, alkyl$S(O)_{n2}$, alkylsulfonyloxy, alkylthioalkyl, alkoxyalkyl, alkoxyalkoxyalkyl, alkylamino and other alkyl-containing groups. Alkyl groups are, for example, methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, isobutyl, tert-butyl and the various isomeric pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl and dodecyl radicals. Preference is given to lower alkyl groups, for example methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, 2-pentyl and 3-pentyl.

There may be mentioned as examples of alkenyl groups vinyl, allyl, methallyl, 1-methylvinyl, but-3-en-2-yl, n-pent-4-enyl and 2-hexen-5-yl; preferably alkenyl radicals having a chain length of from 3 to 5 carbon atoms. Longer chain alkenyl groups may also contain two or more unsaturated C=C bond groups, for example C_2-C_8alkenyl-C_2-C_4alkenyl (for example substituent R_2).

There may be mentioned as examples of alkynyl radicals ethynyl, propargyl, 2-butyn-1-yl, 2-butyn-3-yl, but-2-yn-1-yl, but-3-yn-2-yl, 2-methyl-but-3-yn-2-yl, pent-4-yn-1-yl, hex-4-yn-2-yl and 3-heptyn-2-yl; preferably alkynyl radicals having a chain length of from 3 to 5 carbon atoms.

Suitable haloalkyl radicals include alkyl groups substituted one or more times, especially from one to five times, by halogen, halogen being in particular iodine and especially fluorine, chlorine or bromine, for example fluoromethyl, difluoromethyl, trifluoromethyl, chloromethyl, dichloromethyl, difluorochloromethyl, 1-fluoroethyl, 2-fluoroethyl, 1,1-difluoroethyl, 2,2-difluoroethyl, 2,2,2-trifluoroethyl, 2,2,2-difluorochloroethyl, 2-chloroethyl, 2-bromoethyl, pentafluoroethyl, 2-fluoroprop-1-yl, 3-fluoroprop-1-yl, 3,3-difluoroprop-1-yl and 2,3,3-trifluoroprop-1-yl.

Suitable haloalkenyl radicals include alkenyl groups substituted one or more times by halogen, halogen being in particular bromine or iodine and especially fluorine or chlorine, for example 2- and 3-fluoropropenyl, 2- and 3-chloropropenyl, 2- and 3-bromopropenyl, 2,3,3-trifluoropropenyl, 2,3,3-trichloropropenyl, 4,4,4-trifluorobut-2-en-1-yl and 4-chloro-but-2-en-1-yl. Preferred alkenyl radicals substituted once, twice or three times by halogen are especially those having a chain length of 3 or 5 carbon atoms. The alkenyl groups may be substituted by halogen at saturated or unsaturated carbon atoms and may optionally occur in the *cis* and also *trans* forms.

Suitable haloalkynyl radicals include alkynyl groups substituted one or more times by halogen, halogen being in particular bromine or iodine and especially fluorine or chlorine, for example 3-fluoropropynyl, 3-chloropropynyl, 3-bromopropynyl, 3,3,3-trifluoropropynyl and 4,4,4-trifluoro-but-2-yn-1-yl. Preferred alkynyl groups substituted one or more times by halogen are those having a chain length of from 3 to 5 carbon atoms.

There may be mentioned as examples of cycloalkyl- and halocycloalkyl-containing groups the cyclopropyl, cyclobutyl, cyclopentyl and cyclohexyl group.
Cycloalkylalkyl is, for example, cyclopropylmethyl, dimethylcyclopropylmethyl, difluorocyclopropylmethyl, dichlorocyclopropylmethyl, dibromocyclopropylmethyl, 2,2,3,3-tetrafluorocyclobutylmethyl and 2,2-difluoro-3,3-dichlorocyclobutylmethyl.
The cycloalkyl-containing groups and also any alkylene- or alkenylene-containing groups, for example C_3- or C_4-alkylene or C_3- or C_4-alkenylene bridges, may also be substituted one

or more times by further C_1-C_3alkyl groups, especially methyl groups, and by halogen and C_1-C_3haloalkyl.
The alkylene and alkenylene bridges, for example in the definitions 'R_{15} and R_{14} together form a C_3- or C_4-alkylene bridge' or 'R_{18} and R_{17} together form a C_3- or C_4-alkylene or C_3- or C_4-alkenylene bridge' may, as mentioned in the corresponding definitions, be substituted or unsubstituted.
Likewise, in the definitions 'R_{27} and R_{28} together form a...', 'R_{29} and R_{30} together form a...', 'R_{31} and R_{32} together form a...', and 'R_{41} and R_{40} together form a C_3-C_5alkylene bridge', and 'R_{39} and R_{38} together form a C_2- or C_3-alkylene bridge' and 'R_{57} and R_{56} together form a C_2-C_4alkylene bridge', those alkylene bridges may be substituted by halogen, C_1-C_4alkyl or by C_1-C_3haloalkyl.
Especially in the definitions 'R_{22} and R_{20} together form a ...', 'R_{22} and R_{21} together form a...', 'R_{23} and R_{24} together form a...', 'R_{26} and R_{25} together form a...', 'R_{27} and R_{28} together form a...', 'R_{29} and R_{30} together form a...', 'R_{31} and R_{32} together form a...' and 'R_{41} and R_{40} together form a C_3-C_5alkylene bridge', and also 'R_{39} and R_{38} together form a C_2- or C_3-alkylene bridge' and 'R_{57} and R_{56} together form a C_2-C_4alkylene bridge', a carbon atom of such a bridge may be substituted once or twice, geminally or vicinally, by fluorine.

Alkylsulfonyl is, for example, methylsulfonyl, ethylsulfonyl, propylsulfonyl, isopropylsulfonyl, n-butylsulfonyl, isobutylsulfonyl, sec-butylsulfonyl and tert-butylsulfonyl; preferably methylsulfonyl or ethylsulfonyl.

Haloalkylsulfonyl is, for example, fluoromethylsulfonyl, difluoromethylsulfonyl, trifluoromethylsulfonyl, chloromethylsulfonyl, trichloromethylsulfonyl, 2-fluoroethylsulfonyl, 2,2,2-trifluoroethylsulfonyl and 2,2,2-trichloroethylsulfonyl.

Alkylcarbonyl is, for example, acetyl, propionyl, pivaloyl and n-propylcarbonyl.
Haloalkylcarbonyl is especially chloromethylcarbonyl, bromomethylcarbonyl, trifluoroacetyl, dichloroacetyl, trichloroacetyl, 1-chloroethylcarbonyl, 1-bromoethylcarbonyl and 3,3,3-trifluoropropionyl.

Alkoxy *per se* and alkoxy-containing groups are especially methoxy, ethoxy and propoxy groups.
Alkenyloxy and alkynyloxy *per se* and alkenyloxy- and alkynyloxy-containing groups are especially allyloxy and propargyloxy groups.

Haloalkoxy and haloalkoxy-containing groups are especially the fluoromethoxy, difluoromethoxy, trifluoromethoxy, 2,2,2-trifluoroethoxy, 2-chloroethoxy and 2-fluoroethoxy groups.

Alkoxyalkyl is, for example, methoxymethyl, methoxyethyl, ethoxymethyl, ethoxyethyl, n-propoxymethyl, n-propoxyethyl, isopropoxymethyl and isopropoxyethyl.
Alkenyloxyalkyl is, for example, allyloxy-methyl, methallyloxy-methyl, allyloxy-ethyl and methallyloxy-ethyl.
Haloalkenyloxyalkyl is, for example, 3-chloropropenyloxy-methyl and 3-fluoropropenyloxy-methyl.

Alkynyloxyalkyl is, for example, propargyloxy-methyl, propargyloxy-ethyl, 1-methylpropargyloxy-ethyl and methylpropargyloxy-methyl.
Haloalkynyloxyalkyl is, for example, 3-chloropropynyloxy-methyl and 3-fluoropropynyloxy-methyl.

Alkoxycarbonyl is, for example, methoxycarbonyl, ethoxycarbonyl, n-propoxycarbonyl, isopropoxycarbonyl and n-butoxycarbonyl, preferably methoxycarbonyl and ethoxycarbonyl.
Alkenyloxycarbonyl is, for example, allyloxycarbonyl, methallyloxycarbonyl, 1-propenyloxycarbonyl and (but-2-en-1-yl)oxycarbonyl.
Alkynyloxycarbonyl is, for example, propargyloxycarbonyl, (but-3-yn-2-yl)oxycarbonyl and (2-methyl-but-3-yn-2-yl)oxycarbonyl.

Alkylamino is, for example, methylamino, ethylamino, n-propylamino and isopropylamino.

Alkylthio is, for example, methylthio, ethylthio, propylthio and isopropylthio.
Alkylthioalkyl is, for example, methylthioethyl, ethylthioethyl, methylthiopropyl and ethylthiopropyl.
Haloalkylthio is, for example, fluoromethylthio, difluoromethylthio, trifluoromethylthio, chloromethylthio, 2-fluoroethylthio, 2,2,2-trifluoroethylthio and 2,2,2-trichloroethylthio.
Alkylsulfinyl, alkylsulfinylalkyl, alkylsulfonyl and alkylsulfonylalkyl are, for example, methylsulfinyl, ethylsulfinyl, methylsulfinylethyl, ethylsulfinylethyl, methylsulfonyl, n-propylsulfonyl, methylsulfonylethyl and ethylsulfonylethyl.

Haloalkylsulfinyl is, for example, fluoromethylsulfinyl, difluoromethylsulfinyl, trifluoromethylsulfinyl, chloromethylsulfinyl, trichloromethylsulfinyl, 2-fluoroethylsulfinyl and 2,2,2-trifluoroethylsulfinyl.

Hydroxyalkyl is, for example, 2-hydroxyethyl, 3-hydroxypropyl and 2,3-dihydroxypropyl. Cyanoalkyl is especially cyanomethyl, cyanoethyl, 1-cyanoethyl and 2-cyanopropyl.

A phenyl, benzoyl or heterocyclyl group can be substituted one or more times in dependence upon the substituents indicated; for example, a phenyl or benzoyl ring may be perfluoridated, or carry from 1 to 3 chlorides, alkyl, alkoxy and/or haloalkoxy groups, 1 or 2 bromides and/or nitro groups, and/or 1 cyano and/or haloalkyl group. Heterocyclyl groups may generally be occupied once or twice by the substituents indicated.
A heterocyclyl group may be aromatic and also partially or completely saturated and contain from 1 to 4 nitrogen atoms and/or 1 or 2 oxygen atoms or 1 or 2 sulfur atoms. Examples that may be mentioned include the 2- and 3-pyridyl group, the 2- and 4-pyrimidinyl group, the 1- and 3-pyrazolyl group, the 1- and 2-furyl group, the 1- and 2-thienyl group, the 2-oxazolyl group, the 1-oxadiazolyl group, the 1,2-oxazol-3-yl group, the 1,2-oxazolin-3-yl group, the 1- and 3-triazolyl group, the oxiran-2-yl group, the oxetan-3-yl group, the tetrahydrofur-2-yl group, the tetrahydropyran-2-yl group, the 1,3-dioxazolin-2-yl group, the 1,3-dioxolan-2-yl group and the 1,3-oxathiazol-2-yl group, and also the 4H-pyrido[3,2-b][1,4]oxazin-3-on-2-yl group.

Corresponding meanings may also be given to the substituents in combined definitions, for example alkynylalkenyl, cyanoalkyl, alkoxyalkoxyalkyl, di(alkoxy)alkyl, alkylthioalkyl, alkylsulfinylalkyl, alkylsulfonylalkyl, hydroxyalkyl, alkylcarbonylalkyl, haloalkylcarbonylalkyl, alkoxycarbonylalkyl, alkoxycarbonylhaloalkyl, alkenyloxycarbonylalkyl, alkynyloxycarbonylalkyl, alkylcarbonyloxyalkyl, alkenylcarbonyloxyalkyl, cycloalkylcarbonyloxyalkyl, benzoyloxyalkyl, alkoxycarbonyloxyalkyl, cycloalkylcarbonyloxyalkyl, benzoyloxyalkyl, alkylaminocarbonylalkyl, halocycloalkylalkyl, alkylcarbonylamino, alkylsulfonyloxy and haloalkylsulfonyloxy.
In the definitions of cyanoalkyl, alkylcarbonyl, alkenylcarbonyl, alkoxycarbonyl, alkenyloxycarbonyl, cycloalkylcarbonyl, alkylaminocarbonyl and haloalkylcarbonyl, the carbon atom of the cyano or carbonyl is not included in the lower and upper limits given for the number of carbons in each particular case.

L_1 in the reagents R_{13}-L_1 of formula IX, R_5-L_1 of formula IXb (Reaction Scheme 1) and R_{38}-L_1 of formula IXa, L_2 in the reagent R_2-L_2 of formula IV (Reaction Schemes 1 and 1a), L_3 in the reagent R_{23}-L_3 of formula XVa (Reaction Scheme 5), L_4 in the reagent R_{24}-L_4 of formula XVb (Reaction Scheme 5), L_5 in the reagents R_{22}-L_5 of formula X (Reaction Scheme 4) and R_{26}-L_5 of formula Xa and L_{10} in the reagent R_{102}-L_{10} of formula XVI are leaving groups, for example halogen, especially chlorine, bromine or iodine, or sulfonate, especially $CH_3S(O)_2O$- (mesyloxy) or p-tolyl-$S(O)_2O$- (tosyloxy).
L_6 and L_7 in the reagent of formula XXXVI (Reaction Scheme 8) are leaving groups, for example halogen, especially chlorine or bromine, or, in the case of L_7, also hydroxy or alkoxy.

L_9 in the reagent of formula XII (Reaction Schemes 1f and 22) is a leaving group, for example halogen, especially chlorine or bromine, or sulfonate, especially mesyloxy, tosyloxy or trifluoromethanesulfonyloxy.

L_{11} in the reagent of formula XXV (Reaction Scheme 17) is a leaving group, for example hydroxy, C_1-C_3alkoxy, chlorine, amino or C_1-C_3alkylamino.

L_{12} and L_{13} in the reagents of formulae XXVIa, XXVIb, XXVIc and XXVId (Reaction Scheme 17) are leaving groups, for example chlorine, bromine or iodine, or a sulfonate, especially mesyloxy or tosyloxy.

L_{14} in the reagent of formula XIVa (Reaction Scheme 18) is a leaving group, for example halogen, e.g. chlorine or bromine.

L_{15} in the reagent of formula XVII (Reaction Scheme 18) is a leaving group, for example halogen, especially chlorine, bromine or iodine, or a sulfonate, especially mesyloxy or tosyloxy.

A_0 in the compound of formula IIz (Reaction Scheme 15a) is preferably methyl, chlorine, bromine or carboxy.

A_1 in the compound of formula IIb (Reaction Scheme 1c) is a leaving group, for example halogen, especially fluorine, chlorine or bromine, alkylsulfonyl, especially methylsulfonyl, sulfonate, especially mesyloxy, trifluoromethylsulfonyloxy or phenylsulfonyloxy, or nitro.

A_2 in the compound of formula IIu (Reaction Scheme 1d) is methyl, cyano, formyl, C_1-C_4alkylcarbonyl, carboxyl or C_1-C_4alkoxycarbonyl.

A_3 in the compound of formula IIv (Reaction Scheme 1e) is either a leaving group, for example halogen, especially chlorine or bromine, or a sulfonate group, especially trifluoromethylsulfonyloxy or a C_1-C_4trialkylstannyl or boronic acid group.

B in the reagent B-W of formula V (Reaction Scheme 1e) is, complementarily to A_3 in the compound of formula IIv, either a C_1-C_4trialkylstannyl or a boronic acid group, or a leaving group, for example halogen, especially chlorine or bromine, or a sulfonate group, especially trifluoromethylsulfonyloxy.

Z_1 in the reagent of formula XXXII (Reaction Scheme 15) is a leaving group, for example alkoxy, especially methoxy or ethoxy, or halogen, especially chlorine or bromine.

Z_2 in the reagent of formula XXXII (Reaction Scheme 15) is a leaving group, for example halogen, especially chlorine or bromine, or a sulfonate, especially mesyloxy or phenylsulfonyloxy.

The invention relates also to the salts that the compounds of formula I having acid hydrogen, including especially the carboxylic acid derivatives, for example hydrolysis products of R_2, to which the present invention also relates, are able to form with bases. Those salts are, for example, alkali metal salts, e.g. sodium and potassium salts; alkaline earth metal salts, e.g. calcium and magnesium salts; ammonium salts, *i.e.* unsubstituted ammonium salts and mono- or poly-substituted ammonium salts, e.g. triethylammonium and diisopropylammonium salts; or salts with other organic bases.

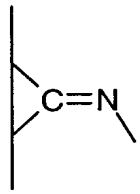
Among the alkali metal and alkaline earth metal hydroxides used as salt formers, emphasis is to be given to, for example, the hydroxides of lithium, sodium, potassium, magnesium and calcium, but especially those of sodium and potassium. Suitable salt formers are described, for example, in WO 97/41112.

Examples of suitable amines for ammonium salt formation that come into consideration are ammonia as well as primary, secondary and tertiary C_1-C_{18}alkylamines, C_1-C_4hydroxyalkyl-amines and C_2-C_4alkoxyalkylamines, for example methylamine, ethylamine, n-propylamine,

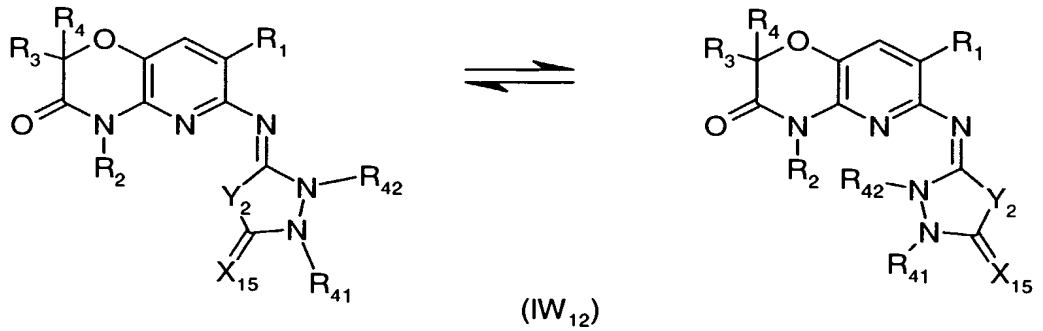
isopropylamine, the four butylamine isomers, n-amylamine, isoamylamine, hexylamine, heptylamine, octylamine, nonylamine, decylamine, pentadecylamine, hexadecylamine, heptadecylamine, octadecylamine, methyl-ethylamine, methyl-isopropylamine, methyl-hexylamine, methyl-nonylamine, methyl-pentadecylamine, methyl-octadecylamine, ethyl-butylamine, ethyl-heptylamine, ethyl-octylamine, hexyl-heptylamine, hexyl-octylamine, dimethylamine, diethylamine, di-n-propylamine, diisopropylamine, di-n-butylamine, di-n-amylamine, diisoamylamine, dihexylamine, diheptylamine, dioctylamine, ethanolamine, n-propanolamine, isopropanolamine, N,N-diethanolamine, N-ethylpropanolamine, N-butyl-ethanolamine, allylamine, n-butenyl-2-amine, n-pentenyl-2-amine, 2,3-dimethylbutenyl-2-amine, dibutenyl-2-amine, n-hexenyl-2-amine, propylenediamine, trimethylamine, triethylamine, tri-n-propylamine, triisopropylamine, tri-n-butylamine, triisobutylamine, tri-sec-butylamine, tri-n-amylamine, methoxyethylamine and ethoxyethylamine; heterocyclic amines, for example pyridine, quinoline, isoquinoline, morpholine, thiomorpholine, piperidine, pyrrolidine, indoline, quinuclidine and azepine; primary arylamines, for example anilines, methoxyanilines, ethoxyanilines, o-, m- and p-toluidines, phenylenediamines, benzidines, naphthylamines and o-, m- and p-chloroanilines; but especially triethylamine, isopropylamine and diisopropylamine.

The presence of an asymmetric carbon atom in the compounds of formula I, for example in the substituent R_2, R_3 and R_4 and also at the R_3- and R_4-carrying oxazine carbon atom and, in general, in alkylsulfinyl groups, wherein R_2, R_3 or R_4 is especially a branched alkyl, alkenyl, haloalkyl, alkoxyalkyl, alkoxycarbonylalkyl or alkylsulfinylalkyl group, means that the compounds may be in the form of optically active individual isomers or in the form of racemic mixtures. In the present invention, 'compounds of formula I' is to be understood as including both the pure optical antipodes and the racemates or diastereoisomers or mixtures thereof.

When an aliphatic C=C double bond is present, for example in alkenyl and haloalkenyl groups of the substituent R_2, geometric <E/Z>-isomerism may occur. Likewise, in the groups

W_{11}, W_{12} and W_{20} the exocyclic double bond  may be present in the syn/anti

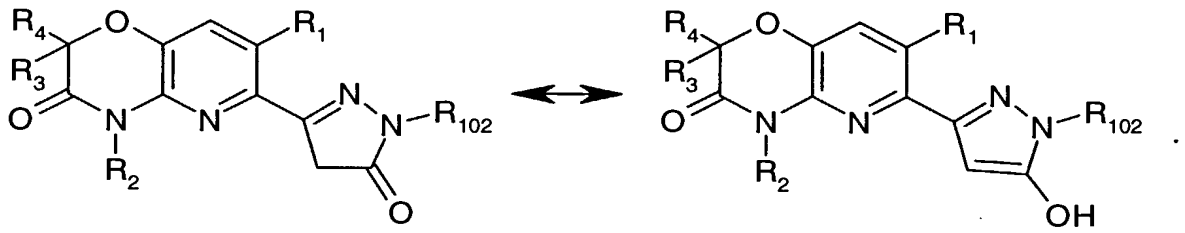
form, as shown by way of example for the compound of formula IW_{12}:



(IW_{12})

Specific <E>- or <Z>-isomers of that kind can, if desired, be isolated in the pure form.

Moreover, for example, the compounds of formulae IW_{100z} and IW_{101z} can, with respect to the groups W_{100} and W_{101}, wherein R_{100} is hydrogen and R_{101} is hydroxy, be present as keto-enol tautomer mixtures; for the group W_{100z} in the compound of formula IW_{100z} by way of example:



(IW_{100z})

The present invention also includes those specific <E>- and <Z>-isomers, or syn- and anti-isomers, and tautomeric forms and mixtures thereof.

Preference is given to compounds of formula I wherein

R_1 is hydrogen, methyl or halogen;

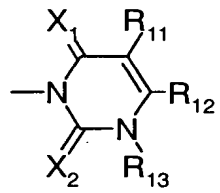
R_2 is hydrogen, C_1-C_{12}alkyl, C_1-C_{12}haloalkyl, C_1-C_{12}alkenyl, C_1-C_{12}alkynyl, C_1-C_{12}haloalkenyl, C_1-C_{12}haloalkynyl, C_1-C_6cycloalkyl-C_1-C_4alkyl, C_1-C_6halocycloalkyl-C_1-C_4alkyl, cyano-C_1-C_{12}alkyl, C_1-C_6alkoxy-C_1-C_4alkyl, C_1-C_4alkoxy-C_1-C_2alkoxy-C_1-C_2alkyl, di(C_1-C_4alkoxy)C_1-C_2alkyl, C_1-C_6alkylthio-C_1-C_4alkyl, C_1-C_6alkylsulfinyl-C_1-C_4alkyl, C_1-C_6alkylsulfonyl-C_1-C_4alkyl, hydroxy-C_1-C_{12}alkyl, C_1-C_6alkylcarbonyl-C_1-C_4alkyl, C_1-C_6haloalkylcarbonyl-C_1-C_4alkyl, C_1-C_6alkoxycarbonyl-C_1-C_4alkyl, C_1-C_6alkoxycarbonyl-C_1-C_4haloalkyl, C_1-C_6alkoxycarbonyl-benzyl, C_1-C_6alkenyloxycarbonyl-C_1-C_4alkyl, C_1-C_6alkynyloxycarbonyl-C_1-C_4alkyl, C_1-C_6alkylcarbonyloxy-C_1-C_4alkyl, C_1-C_6alkenylcarbonyloxy-C_1-C_4alkyl, C_1-C_6cycloalkylcarbonyloxy-C_1-C_4alkyl, benzoyloxy-C_1-C_4alkyl, C_1-C_6alkoxycarbonyloxy-C_1-C_4alkyl, C_1-C_6alkylaminocarbonyl-C_1-C_4alkyl, C_1-

C_6alkylaminocarbonyl-benzyl, or C_1-C_4alkyl substituted by phenyl or by heterocyclyl, wherein the phenyl and heterocyclyl group may be substituted one or more times by halogen, C_1-C_6alkyl, C_1-C_6haloalkyl, C_1-C_6alkenyl, C_1-C_6alkynyl, C_1-C_6haloalkenyl, C_1-C_6haloalkynyl, C_1-C_6cycloalkyl-C_1-C_4alkyl, C_1-C_6halocycloalkyl-C_1-C_4alkyl, cyano-C_1-C_{12}alkyl, C_1-C_6alkoxy-C_1-C_4alkyl, C_1-C_6alkylthio-C_1-C_4alkyl, C_1-C_6alkylsulfinyl-C_1-C_4alkyl, C_1-C_6alkylsulfonyl-C_1-C_4alkyl, hydroxy-C_1-C_{12}alkyl, C_1-C_6alkylcarbonyl-C_1-C_4alkyl, C_1-C_6alkoxycarbonyl-C_1-C_4alkyl, C_1-C_6alkoxycarbonyl-C_1-C_4haloalkyl, C_1-C_6alkylcarbonyloxy-C_1-C_4alkyl, C_1-C_6alkoxycarbonyloxy-C_1-C_4alkyl, C_1-C_4alkoxy-C_1-C_2alkoxy-C_1-C_2alkyl or by phenyl;

R_3 is hydrogen, C_1-C_{12}alkyl, C_1-C_{12}haloalkyl or unsubstituted or substituted phenyl;

R_4 is hydrogen or C_1-C_6alkyl;

W is a group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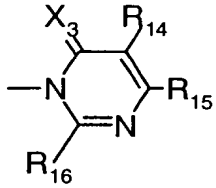
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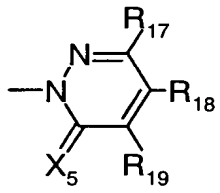
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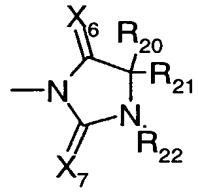
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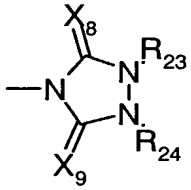
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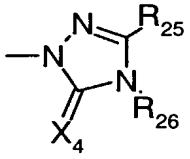
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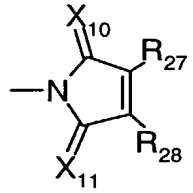
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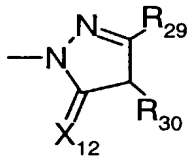
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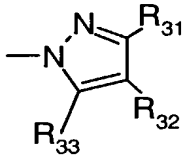
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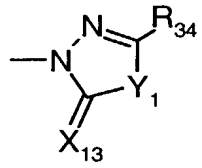
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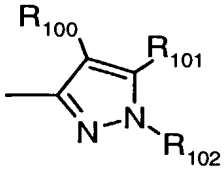
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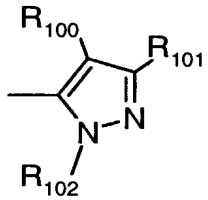
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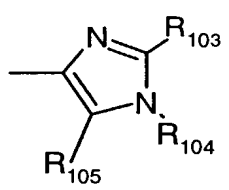

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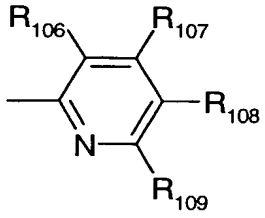

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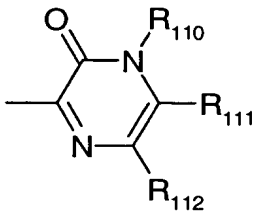
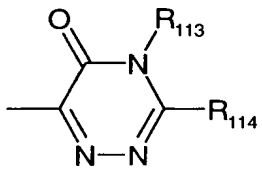
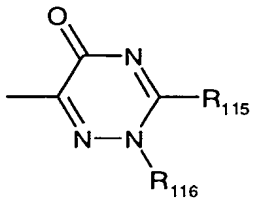


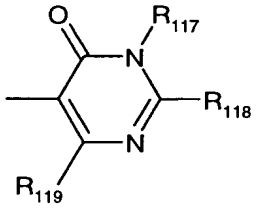
(W104),



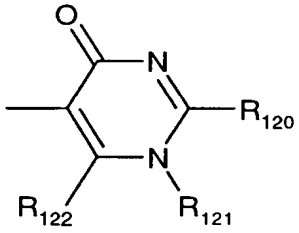
(W105),



(W106),



(W107) or



(W108);

R_{11} is hydrogen, C_1-C_3alkyl, halogen, C_1-C_3haloalkyl or cyano;

R_{12} is C_1-C_3alkyl, C_1-C_3haloalkyl, C_1-C_3alkyl-$S(O)_{n1}$-, C_1-C_3haloalkyl-$S(O)_{n1}$- or cyano; and

R_{13} is C_1-C_3alkyl, C_1-C_3haloalkyl or amino; or

R_{12} and R_{11} or R_{12} and R_{13} together form a C_3- or C_4-alkylene bridge which may be substituted by halogen, C_1-C_3haloalkyl or by cyano;

R_{14} is hydrogen, C_1-C_3alkyl, halogen, C_1-C_3haloalkyl or cyano; and

R_{15} is C_1-C_3alkyl, C_1-C_3haloalkyl, C_1-C_3alkyl-$S(O)_{n2}$-, C_1-C_3haloalkyl-$S(O)_{n2}$- or cyano; or

R_{15} and R_{14} together form a C_3- or C_4-alkylene bridge which may be substituted by halogen, C_1-C_3haloalkyl or by cyano;

R_{16} is hydrogen, C_1-C_3alkyl, halogen, C_1-C_3haloalkyl, C_1-C_3alkoxy, C_1-C_3haloalkoxy, C_1-C_3alkylthio, C_1-C_3alkylsulfinyl, C_1-C_3alkylsulfonyl or cyano;

n_1 and n_2 are 0, 1 or 2;

R_{17} is hydrogen, C_1-C_3alkyl, halogen or cyano; and

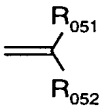
R_{18} is C_1-C_3alkyl, halogen, C_1-C_3haloalkyl, C_1-C_3alkylthio, C_1-C_3alkylsulfinyl, C_1-C_3alkylsulfonyl or cyano; or

R_{18} and R_{17} together form a C_3- or C_4-alkylene or C_3- or C_4-alkenylene bridge, both of which may be substituted by halogen, C_1-C_3alkyl or by C_1-C_3haloalkyl;

R_{19} is hydrogen, halogen, C_1-C_3alkyl or amino; or

R_{19} and R_{18} together form a C_3- or C_4alkylene or C_3- or C_4-alkenylene bridge, both of which may be substituted by halogen, C_1-C_3alkyl or C_1-C_3haloalkyl;

R_{20} and R_{21} are each independently of the other hydrogen or C_1-C_4alkyl; or

R_{20} and R_{21} together are a group  ;

R_{051} and R_{052} are each independently of the other C_1-C_4alkyl; or

R_{051} and R_{052} together form a C_4- or C_5-alkylene bridge;

R_{051} and R_{22} together form a C_3alkylene bridge;

R_{22} is hydrogen or C_1-C_3alkyl; or

R_{22} and R_{20} or R_{22} and R_{21} together form a C_3-C_5alkylene bridge which may be interrupted by oxygen or by –C(O)- and/or substituted by halogen, C_1-C_4alkyl, C_1-C_3haloalkyl, C_2-C_4alkenyl, C_1-C_3alkoxycarbonyl, C_1-C_3alkylcarbonyloxy, C_1-C_3alkylsulfonyloxy or by hydroxy;

R_{23} is hydrogen, C_1-C_3alkyl or C_1-C_3haloalkyl; or

R_{23} and R_{24} together form a C_3-C_5alkylene bridge which may be interrupted by oxygen, sulfur, -S(O)-, -$S(O)_2$- or by -C(O)-;

R_{25} is hydrogen, halogen, C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4alkoxy, C_1-C_4haloalkoxy, C_1-C_4alkylthio, C_1-C_4haloalkylthio, C_1-C_4alkylsulfinyl, C_1-C_4haloalkylsulfinyl, C_1-C_4alkylsulfonyl, C_1-C_4haloalkylsulfonyl or cyano; and

R_{26} is hydrogen, C_1-C_4alkyl or C_1-C_4haloalkyl; or

R_{26} and R_{25} together form a C_3-C_5alkylene bridge which may be interrupted by oxygen or by -C(O)- and/or substituted by halogen, C_1-C_4alkyl, C_1-C_3haloalkyl, C_2-C_4alkenyl, C_1-C_3alkoxy-carbonyl, C_1-C_3alkylcarbonyloxy, C_1-C_3alkylsulfonyloxy or by hydroxy;

R_{27} and R_{28} are each independently of the other hydrogen or C_1-C_4alkyl; or

R_{27} and R_{28} together form a C_3-C_5alkylene bridge or a C_4alkenylene bridge which may be interrupted by oxygen, sulfur, -S(O)-, -$S(O)_2$- or by -C(O)-;

R_{29} and R_{30} are each independently of the other hydrogen or C_1-C_4alkyl; or

R_{29} and R_{30} together form a C_3-C_5alkylene bridge which may be interrupted by oxygen, sulfur, -S(O)-, -$S(O)_2$- or by -C(O)-;

R_{31} is hydrogen, C_1-C_4alkyl or C_1-C_4haloalkyl; and

R_{32} is hydrogen, C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4alkylthio, C_1-C_4alkylsulfinyl, C_1-C_4alkyl-sulfonyl, cyano or nitro; or

R_{31} and R_{32} together form a C_3-C_5alkylene bridge which may be interrupted by oxygen, sulfur, -S(O)-, -$S(O)_2$- or by -C(O)-;

R_{33} is hydrogen, C_1-C_3alkyl, halogen, C_1-C_3haloalkyl, C_1-C_3alkoxy, C_1-C_3haloalkoxy, C_1-C_3alkylthio, C_1-C_3alkylsulfinyl, C_1-C_3alkylsulfonyl, amino, C_1-C_3alkylamino, C_1-C_3alkylcarbonylamino, C_1-C_3haloalkylcarbonylamino or cyano;

R_{34} is C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4alkoxy or C_1-C_4alkylthio;

R_{100} is hydrogen, halogen, nitro, amino, cyano, C_1-C_3alkyl, C_2- or C_3-alkenyl or C_2- or C_3-alkynyl;

R_{101} is hydrogen, halogen, nitro, amino, cyano, hydroxy, mercapto, C_1-C_3alkyl, C_1-C_3haloalkyl, C_2- or C_3-alkenyl, C_2- or C_3-alkynyl, C_1-C_3alkoxy, C_1-C_3haloalkoxy, C_1-C_3alkylthio, C_1-C_3alkylsulfinyl, C_1-C_3alkylsulfonyl, C_1-C_3haloalkylthio, C_1-C_3haloalkylsulfinyl, C_1-C_3haloalkylsulfonyl, $FS(O)_2$-, $ClS(O)_2$-, C_1-C_6alkylsulfonyloxy, C_1-C_6haloalkylsulfonyloxy, C_1-C_3alkylcarbonyl, HC(O)-, HOC(O)-, ClC(O)-, FC(O)-, C_1-C_3alkoxycarbonyl, $H_2NC(O)$- or $H_2NC(S)$-;

R_{102} is hydrogen, C_1-C_6alkyl, C_3-C_6alkenyl, C_3-C_6alkynyl, C_3-C_6cycloalkyl, C_1-C_6haloalkyl, C_1-C_3alkylsulfonyl, or C_1-C_6alkyl which may be substituted by cyano, HO-, HOC(O)-, C_1-C_3-alkoxycarbonyl or by HC(O)-; or,

when W is a group W_{100},

R_{102} and R_{101} together form a C_3-C_5alkylene bridge which may be interrupted by oxygen, sulfur, -S(O)-, $-S(O)_2$- or by -C(O)- and/or substituted by hydroxy or by halogen;

R_{103} is as defined for R_{101};

R_{104} is as defined for R_{102};

R_{105} is as defined for R_{100};

R_{106} is hydrogen, halogen, amino, nitro, hydroxy, C_1-C_3alkyl or C_1-C_3alkoxy;

R_{107} is hydrogen, halogen, amino, hydroxy, C_1-C_3alkyl, C_1-C_3haloalkyl, HC(O)-, HOC(O)-, hydroxy-C_1-C_3alkyl, C_1-C_3alkoxy or C_1-C_3haloalkoxy; and

R_{108} is hydrogen, halogen, nitro, amino, cyano, HC(O)-, HOC(O)-, $H_2NC(O)$-, $H_2NC(S)$-, hydroxy, HS-, C_1-C_3alkyl, C_1-C_3haloalkyl, C_2- or C_3-alkenyl, C_1-C_3alkoxy, C_1-C_3haloalkoxy, C_1-C_3alkylcarbonyl, C_1-C_3alkoxycarbonyl, C_1-C_3alkylthio, C_1-C_3haloalkylthio, C_1-C_3alkylsulfinyl, C_1-C_3haloalkylsulfinyl, C_1-C_3alkylsulfonyl, C_1-C_3haloalkylsulfonyl, C_1-C_3alkylsulfonyloxy or C_1-C_3haloalkylsulfonyloxy;

R_{109} is as defined for R_{107};

R_{107} and R_{108} together form a C_3-C_5alkylene bridge which may be interrupted by oxygen, sulfur, -S(O)-, $-S(O)_2$- or by -C(O)- and/or substituted by hydroxy or by halogen;

R_{108} and R_{109} together form a C_3-C_5alkylene bridge which may be interrupted by oxygen, sulfur, -S(O)-, $-S(O)_2$- or by -C(O)- and/or substituted by hydroxy or by halogen;

R_{110} is hydrogen, C_1-C_3alkyl, C_1-C_3haloalkyl, C_3-C_4alkenyl or C_3-C_4alkynyl;

R_{111} is as defined for R_{108};

R_{112} is as defined for R_{109};

R_{111} and R_{112} together form a C_3-C_5alkylene bridge which may be interrupted by oxygen, sulfur, -S(O)-, -$S(O)_2$- or by -C(O)- and/or substituted by hydroxy or by halogen;

R_{110} and R_{111} together form a C_3-C_5alkylene bridge which may be interrupted by oxygen, sulfur, -S(O)-, -$S(O)_2$- or by -C(O)- and/or substituted by hydroxy or by halogen, wherein a CH_2 group is bonded to the N atom of the pyrazinone;

R_{113} is as defined for R_{110};

R_{114} is as defined for R_{108};

R_{113} and R_{114} together form a C_3-C_5alkylene bridge which may be interrupted by oxygen, sulfur, -S(O)-, -$S(O)_2$- or by -C(O)- and/or substituted by hydroxy or by halogen, wherein a CH_2 group is bonded to the N atom of the triazinone;

R_{115} is as defined for R_{108};

R_{116} is as defined for R_{110};

R_{115} and R_{116} together form a C_3-C_5alkylene bridge which may be interrupted by oxygen, sulfur, -S(O)-, -$S(O)_2$- or by -C(O)- and/or substituted by hydroxy or by halogen, wherein a CH_2 group is bonded to the N atom of the triazinone;

R_{117} is as defined for R_{110};

R_{118} is as defined for R_{108};

R_{119} is as defined for R_{106};

R_{117} and R_{118} together form a C_3-C_5alkylene bridge which may be interrupted by oxygen, sulfur, -S(O)-, -$S(O)_2$- or by -C(O)- and/or substituted by hydroxy or by halogen, wherein a CH_2 group is bonded to the N atom of the pyrimidinone;

R_{120} is as defined for R_{108};

R_{121} is as defined for R_{110};

R_{122} is as defined for R_{106};

R_{121} and R_{120} together form a C_3-C_5alkylene bridge which may be interrupted by oxygen, sulfur, -S(O)-, -$S(O)_2$- or by -C(O)- and/or substituted by hydroxy or by halogen, wherein a CH_2 group is bonded to the N atom of the pyrimidinone;

X_1, X_2, X_3, X_4, X_5, X_6, X_7, X_8, X_9, X_{10}, X_{11}, X_{12} or X_{13} are each independently of the others oxygen or sulfur; and

Y_1 is oxygen or sulfur.

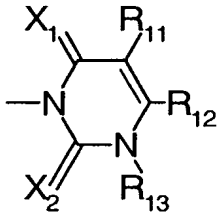
Preference is also given to compounds of formula I wherein R_1 is hydrogen or fluorine.

In further preferred compounds of formula I, R_2 is hydrogen, methyl, ethyl, n-propyl, isopropyl, 2-methylpropyl, 3-methylpropyl, n-butyl, 2-butyl, 3-methyl-but-1-yl, 2-pentyl, 3-pentyl, allyl, 1-methyl-prop-2-en-1-yl, 2-methyl-prop-2-en-1-yl, 3-methyl-prop-2-en-1-yl, 2-buten-1-yl, 3-buten-1-yl, 1-buten-3-yl, 4-penten-1-yl, propargyl, 1-butyn-3-yl, 2,2,2-trifluoroethyl, 2-chloroethyl, 3-fluoroprop-1-yl, 3-chloroprop-1-yl, 3-chloro-2-methylprop-1-yl, 4-chlorobut-1-yl, 1-chloro-prop-1-en-3-yl, 2-chloro-prop-1-en-3-yl, 3-chloro-but-2-en-1-yl, 5-chloropentyl, 2-bromo-prop-1-en-3-yl, 6,6-dimethyl-hept-2-en-4-yn-1-yl, dimethylethylsilylmethyl, trimethylsilylmethyl-prop-2-en-1-yl, cyclopropylmethyl, dichlorocyclopropylmethyl, cyanoethyl, methoxyethyl, ethoxyethyl, ethylthioethyl, 2,2-dimethoxyethyl, 3,3-dimethoxypropyl, ethylcarbonylmethyl, tert.-butylcarbonylmethyl, cyclopropylcarbonylmethyl, oxiranylmethyl, methoxycarbonylmethyl, ethoxycarbonylmethyl, 1-(methoxycarbonyl)-ethyl, 1-(ethoxycarbonyl)-ethyl, 1-(methoxycarbonyl)-prop-1-yl, benzyl or 2-methoxybenzyl; R_3 is hydrogen, methyl, ethyl, n-propyl or n-butyl; and R_4 is hydrogen or methyl.

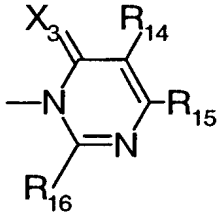
In a selected group of compounds of formula I, W is a group W_1 to W_{21}. Of those compounds, special preference is given to those wherein W is a group W_1, W_2, W_4, W_5, W_7, W_{11}, W_{12}, W_{14}, W_{15}, W_{18} or W_{21}. Of those compounds, very special preference is given to those wherein W is a group W_1, W_2, W_4, W_5, W_7 or W_{11}.

In a further selected group of compounds of formula I, W is a group W_3, W_6, W_8, W_9, W_{10}, W_{13}, W_{16}, W_{17} or W_{19}.

In a preferred group of compounds of formula I, W is a group W_1 or W_2



(W_1) or

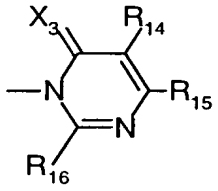


(W_2)

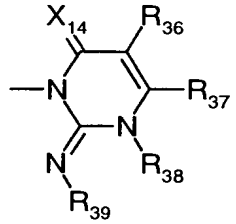
wherein R_{11}, R_{12}, R_{13}, R_{14}, R_{15}, R_{16}, X_1, X_2 and X_3 are as defined for formula I. Of those compounds, special preference is given to those wherein X_1 and X_3 are oxygen; R_{11} and R_{14} are hydrogen, chlorine or methyl; R_{12} and R_{15} are methyl, ethyl, chlorodifluoromethyl, trifluoromethyl, pentafluoroethyl or cyano; R_{13} is methyl, fluoromethyl, propargyl or amino; and R_{16} is chlorine, methoxy, fluoromethoxy or methylthio.
Of those compounds, very special preference is given to those wherein X_1, X_2 and X_3 are oxygen; R_{11} and R_{14} are hydrogen or methyl; R_{12} and R_{15} are trifluoromethyl,

pentafluoroethyl or cyano; R_{13} is methyl or amino; and R_{16} is chlorine or methoxy. Of those compounds, preference is given more especially to those wherein W is a group W_1; R_{11} is hydrogen; R_{12} is trifluoromethyl; and R_{13} is methyl, fluoromethyl or amino.

In a further preferred group of compounds of formula I, W is a group W_2 or W_{11}



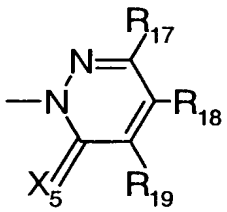
(W_2) or



(W_{11})

wherein R_{14}, R_{15}, R_{36}, R_{37}, R_{38}, R_{39}, X_3 and X_{14} are as defined for formula I; and R_{16} is amino, C_1-C_3alkylamino, di(C_1-C_3alkyl)amino, allylamino or propargylamino. Of those compounds, special preference is given to those wherein X_3 and X_{14} are oxygen; R_{14} and R_{36} are hydrogen, chlorine or methyl; R_{15} and R_{37} are methyl, ethyl, chlorodifluoromethyl, trifluoromethyl, pentafluoroethyl or cyano; R_{16} is amino or methylamino; and R_{39} and R_{38} together form an unsubstituted or methyl-substituted C_2alkylene or C_2alkenylene bridge. Of those compounds, very special preference is given to those wherein R_{15} and R_{37} are trifluoromethyl.

In another preferred group of compounds of formula I, W is a group W_3

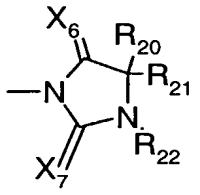


(W_3)

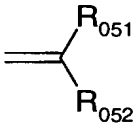
wherein R_{17}, R_{18}, R_{19} and X_5 are as defined for formula I. Special preference is given especially to those wherein R_{17} is hydrogen or C_1-C_3alkyl; R_{18} is trifluoromethyl or methylsulfonyl; R_{19} is hydrogen, C_1-C_3alkyl or amino; and X_5 is oxygen. Of those compounds, very special preference is given to those wherein R_{17} is hydrogen; and R_{19} is methyl or amino.

Special preference is given to compounds of formula I wherein W is a group W_3; R_{17} and R_{19} are each independently of the other hydrogen or methyl; and R_{18} is trifluoromethyl, pentafluoroethyl or cyano. Very special preference is given especially to those wherein R_{17} is hydrogen; R_{18} is trifluoromethyl; and R_{19} is hydrogen or methyl.

Preference is also given to compounds of formula I wherein W is the group W_4



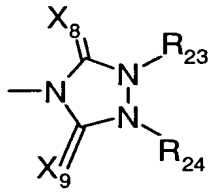
(W_4),

R_{20}, R_{21} and R_{22} are as defined for formula I, and X_6 and X_7 are oxygen. Of those compounds, special preference is given especially to those wherein R_{21} and R_{22} together form a C_3- or C_4-alkylene bridge which is substituted once or twice by fluorine or chlorine or once by hydroxy or is interrupted by a keto group. Special preference is also given to those compounds wherein R_{20} and R_{21} together are a group  ; R_{051} is hydrogen; and

R_{052} and R_{22} together form a C_3alkylene bridge.

In an especially preferred group of compounds, W is a group W_4 wherein R_{20} is hydrogen; and R_{21} and R_{22} together form a C_4alkylene group which is unsubstituted or substituted once or twice by fluorine or chlorine.

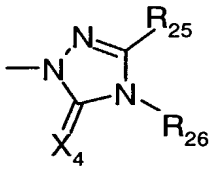
Preference is also given to compounds of formula I wherein W is the group W_5



(W_5) ,

R_{23} and R_{24} are as defined for formula I; and X_8 and/or X_9 are oxygen. Of those compounds, special preference is given to those wherein R_{23} and R_{24} together form a C_3-C_5alkylene bridge which may be interrupted by oxygen. Very special preference is given to those wherein R_{23} and R_{24} together form a C_3- or C_4-alkylene bridge.

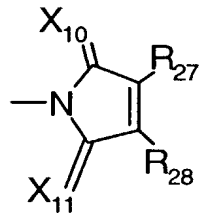
In another preferred group of compounds of formula I, W is a group W_6



(W_6)

wherein R_{25} and R_{26} are as defined for formula I; and X_4 is oxygen. Of those compounds, special preference is given to those wherein R_{25} and R_{26} together form a C_4alkylene bridge. In another especially preferred group, W is a group W_6; R_{25} is methyl, ethyl or trifluoromethyl; and R_{26} is methyl or difluoromethyl. Of those compounds, very special preference is given to those wherein X_4 is oxygen.

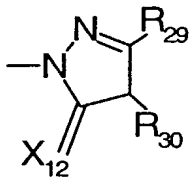
In a further preferred group of compounds of formula I, W is a group W_7



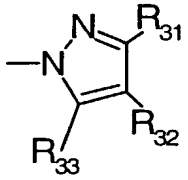
(W_7)

wherein R_{27} and R_{28} are as defined for formula I; and X_{10} and X_{11} are oxygen. Of those compounds, special preference is given to those wherein R_{27} and R_{28} together form a C_4alkylene bridge. Special preference is likewise given to those compounds wherein R_{27} is methyl and R_{28} is C_1-C_3alkyl.

In other preferred groups of compounds of formula I, W is a group W_8 or W_9



(W_8) or

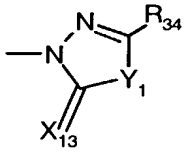


(W_9)

wherein R_{29}, R_{30}, R_{31}, R_{32} and R_{33} are as defined for formula I; and X_{12} is oxygen. Of those compounds, special preference is given to those wherein R_{29} and R_{30} together and R_{31} and R_{32} together form, in each case, a C_4alkylene bridge. Of those groups, very special preference is given especially to those wherein W is a group W_9 and R_{33} is chlorine or bromine.

In a further group of preferred compounds, W is a group W_9 wherein R_{31} is hydrogen, chlorine, methyl or trifluoromethyl; R_{32} is methyl, trifluoromethyl, methylthio, methylsulfinyl, methylsulfonyl, cyano or nitro; and R_{33} is chlorine, amino, methylamino or ethylamino.

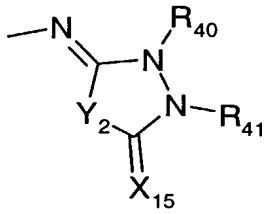
In another preferred group of compounds of formula I, W is a group W_{10}



(W_{10})

wherein X_{13} is oxygen; and R_{34} and Y_1 are as defined for formula I. Of those compounds, special preference is given to those wherein R_{34} is tert-butyl or trifluoromethyl.

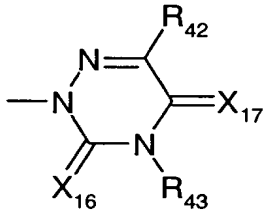
Preference is likewise given to compounds of formula I wherein W is a group W_{12}



(W_{12}),

X_{15} is oxygen; Y_2 is sulfur; R_{40} is methyl or ethyl; and R_{41} is methyl, ethyl or difluoromethyl; or R_{40} and R_{41} together form a $-(CH_2)_3-$, $-CH_2CH(CH_3)CH_2-$, $-(CH_2)_4-$, $-CH_2CH_2OCH_2-$ or $-CH_2CH_2OCH_2CH_2-$ bridge.

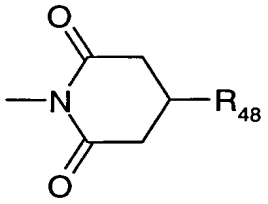
In a further preferred group of compounds of formula I, W is a group W_{13}



(W_{13}),

R_{42} is hydrogen or cyano; R_{43} is methyl; and X_{16} and X_{17} are oxygen.

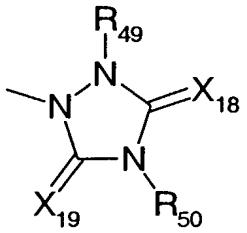
In a further preferred group of compounds of formula I, W is a group W_{15}



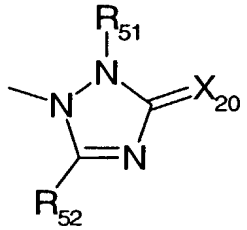
(W_{15}).

Of those compounds, special preference is given to those wherein R_{48} is trifluoromethyl.

Preference is also given to compounds of formula I wherein W is a group W_{16} or W_{17}



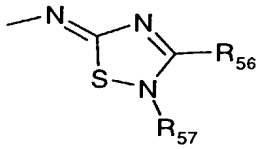
(W_{16}) or



(W_{17}),

X_{18} and X_{20} are oxygen; R_{49} is methyl; R_{50} is methyl or difluoromethyl; and R_{52} is chlorine or methyl.

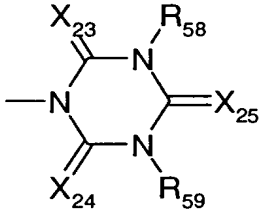
Preference is also given to compounds of formula I wherein W is a group W_{20}



(W_{20}),

and R_{56} and R_{57} together form a $-SCH_2CH_2-$, $-SCH(CH_3)CH_2-$, $-SC(CH_3)_2CH_2-$, $-SCH_2CH_2CH_2-$, $-(CH_2)_3-$, $-CH_2CH(CH_3)CH_2-$ or $-CH_2C(CH_3)_2CH_2-$ bridge.

In a further preferred group of compounds of formula I, W is a group W_{21}

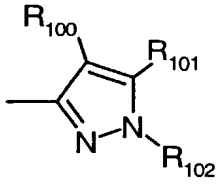


(W_{21}),

R_{58} is methyl or amino; R_{59} is methyl; and X_{23} and X_{24} are oxygen.

In another selected group of compounds of formula I, W is a group W_{100}, W_{101}, W_{102}, W_{103}, W_{104}, W_{105}, W_{106}, W_{107}, W_{108} or W_{109}, especially the group W_{100}.

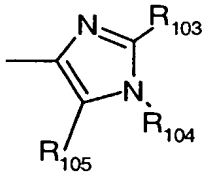
Very special preference is given to those compounds of formula I wherein W is a group W_{100}



(W_{100}),

R_{100} is methyl, chlorine or bromine; R_{101} is chlorine, bromine, trifluoromethyl, difluoromethoxy, methylsulfonyl, ethylsulfonyl or cyano; and R_{102} is methyl or ethyl; or R_{102} and R_{101} together form a C_4alkylene bridge.

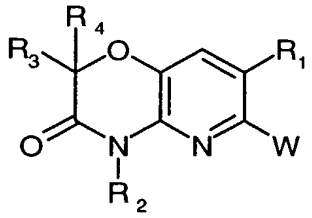
Preference is also given to compounds of formula I wherein W is a group W_{102}



(W_{102}) ,

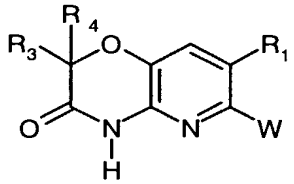
R_{103} is methyl, ethyl or trifluoromethyl; and R_{104} is methyl, ethyl or difluoromethyl; or R_{104} and R_{103} together form a C_4alkenylene bridge; and R_{105} is methyl, chlorine or bromine.

The process according to the invention for the preparation of compounds of formula I according to variant a) and Reaction Scheme 1a is carried out analogously to known processes, as described, for example, in WO 98/42698, and comprises, for the preparation of those compounds of formula I



(I)

wherein R_1, R_2, R_3, R_4 and W are as defined for formula I with the exception of R_2 as hydrogen, reacting a compound of formula Ia



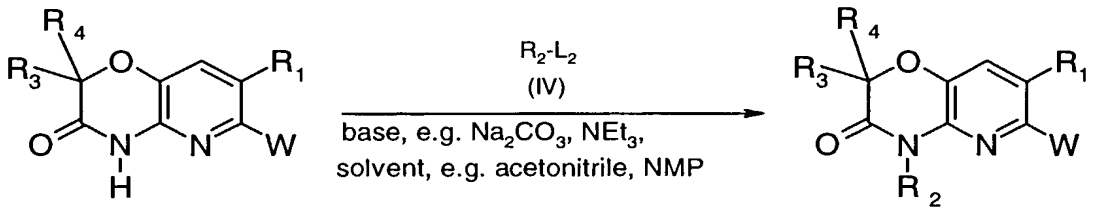
(Ia) ,

wherein R_1, R_3, R_4 and W are as defined, with a suitable alkylating reagent of formula IV

R_2-L_2 (IV),

wherein R_2 is as defined for formula I with the exception of R_2 as hydrogen, and L_2 is a leaving group, for example halogen, especially chlorine, bromine or iodine, or a sulfonate, especially $CH_3S(O)_2O$- (mesyloxy) or p-tolyl-$S(O)_2O$- (tosyloxy), in the presence of a base and, optionally, one or more catalysts preferably in an inert diluent at temperatures of from -20° to 250°C, preferably from 20°C to the boiling point of the solvent or alkylating agent used, and at normal pressure or optionally under a slightly elevated pressure.

Reaction Scheme 1a:

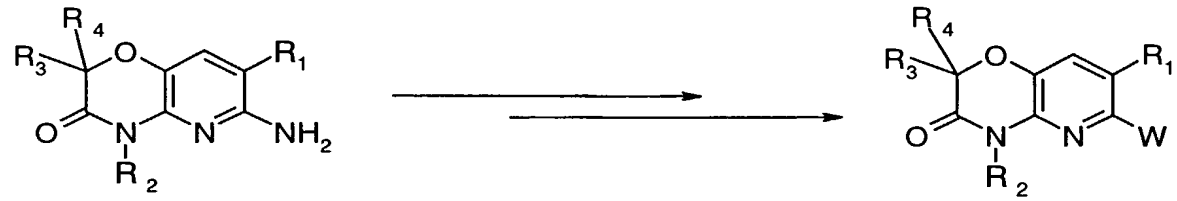


(IIa) (I): (R_2 other than hydrogen, W=W_1-W_{21}, W_{100}-W_{109})

Bases that are suitable for that alkylating reaction are, for example, alkali or alkaline earth metal hydrides, especially sodium hydride; alkali or alkaline earth metal carbonates, especially sodium hydrogen carbonate or sodium or potassium carbonate; trialkylamines, especially triethylamine or ethyl-diisopropylamine; aromatic amines, especially pyridine or N,N-dimethylaminopyridine; or caesium fluoride. Suitable catalysts are, for example, crown ethers, especially 15-crown-5 or 18-crown-6; alkali metal halides, especially sodium or potassium iodide; or copper(I) iodide. Suitable diluents are, for example, aromatic or heteroaromatic hydrocarbons, for example toluene, one of the xylene isomers, or 5-ethyl-2-methylpyridine; ketones, especially acetone or methyl ethyl ketone; ethers, especially tetrahydrofuran (THF), dimethoxyethane or diethoxymethane; esters, especially ethyl acetate; nitriles, especially acetonitrile; amides, especially N,N-dimethylformamide (DMF) or N-methylpyrrolidone (NMP); or sulfoxides, especially dimethyl sulfoxide.

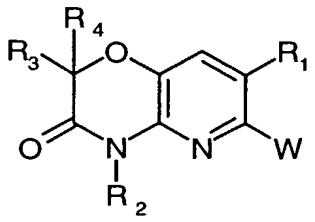
The process according to the invention for the preparation of compounds of formula I according to variant b) and Reaction Scheme 1b

Reaction Scheme 1b:



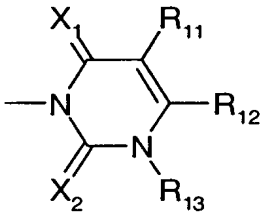
(IIa) (I): (W_1-W_{21}, W_{100}-W_{109})

is carried out analogously to known processes, as described, for example, in WO 99/52892, WO 99/52893 and WO 98/27083, and comprises, for the preparation of those compounds of formula I



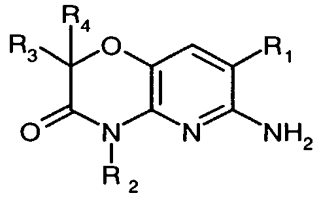
(I)

wherein R_1, R_2, R_3 and R_4 are as defined for formula I and W is a group W_1



(W_1),

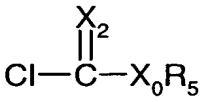
wherein R_{11}, R_{12}, R_{13}, X_1 and X_2 are as defined for formula I, reacting a compound of formula IIa



(IIa) ,

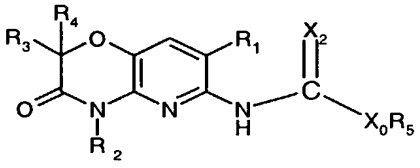
wherein R_1, R_2, R_3 and R_4 are as defined, either

1), according to route a) in Reaction Scheme 1, with a compound of formula VI



(VI),

wherein X_2 is as defined for formula I, X_0 is oxygen, sulfur or amino, and R_5 is C_1-C_4alkyl, to yield the compound of formula IIc



(IIc) ,

wherein R_1, R_2, R_3, R_4, R_5, X_0 and X_2 are as defined, or, as a variant thereof and in cases where X_0 in the compound of formula IIc is sulfur, first of all 1) carrying out a reaction with the reagent of formula XIn

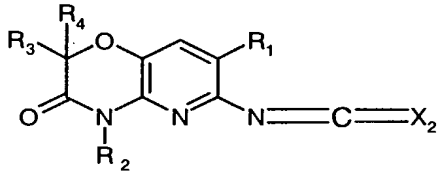
$$X_2=C=S \qquad \text{(XIn)}$$

and then 2) with the alkylating reagent of formula IXb

R_5-L_1 (IXb)

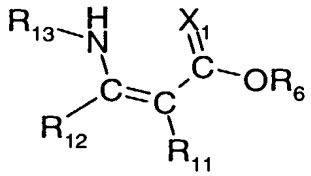
to yield the compound of formula IIc, the substituents X_2 and R_5 in the reagents of formulae XIn and IXb being as defined and L_1 being a leaving group, for example halogen, especially chlorine, bromine or iodine, or sulfonate, especially mesyloxy or tosyloxy, or

2), according to route b) in Reaction Scheme 1, carrying out treatment with (thio-)phosgene or oxalyl chloride to yield the compound of formula IId



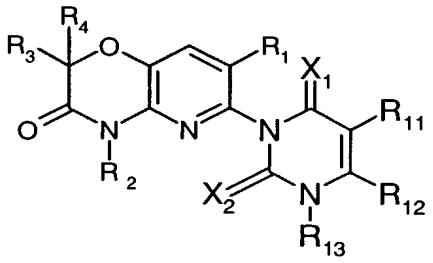
(IId) ,

wherein R_1, R_2, R_3, R_4 and X_2 are as defined, and then, according to route c) in Reaction Scheme 1, condensing and cyclising the resulting compounds of formulae IIc and IId with an enamine of formula VII



(VII),

wherein R_{11}, R_{12} and R_{13} are as defined, X_1 is oxygen or sulfur, and R_6 is C_1-C_4alkyl, in the presence of from 0.01 to 1.5 equivalents of a suitable base, for example an alkali metal hydroxide or hydride, e.g. sodium hydroxide or sodium hydride, or an alcoholate, e.g. sodium ethanolate or potassium tert-butanolate, in an inert solvent, for example an aromatic hydrocarbon, e.g. toluene or one of the xylene isomers, a nitrile, e.g. acetonitrile, or an amide, e.g. DMF or NMP (see also Example P4), to form the compound of formula IW_1

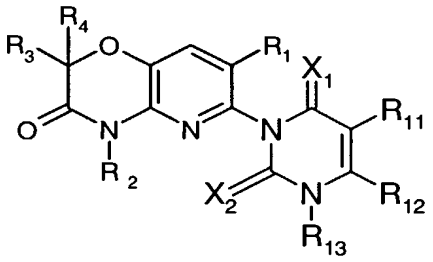


(IW_1) ,

wherein R_1, R_2, R_3, R_4, R_{11}, R_{12}, R_{13}, X_1 and X_2 are as defined, and

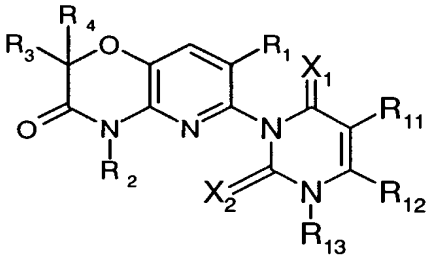
3) optionally, further functionalising those compounds according to the definition of R_1, R_2, R_{11}, R_{13}, X_1 and X_2 for formula I according to standard methods (Reaction Scheme 1). Examples of such standard methods for further functionalisation are:

aa) thionation of compounds of formula IW_1



(IW$_1$),

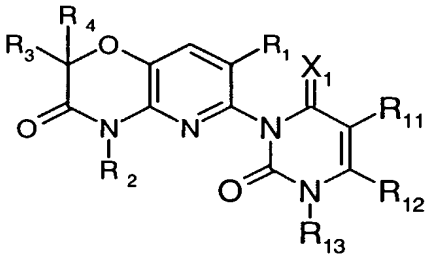
wherein R_1, R_2, R_3, R_4, R_{11}, R_{12} and R_{13} are as defined for formula I and X_1 and/or X_2 are oxygen, with the aid of a thionating reagent, for example Lawesson's reagent or P_2S_5 (phosphorus pentasulfide), to form the compound of formula IW_1



(IW$_1$),

wherein R_1, R_2, R_3, R_4, R_{11}, R_{12} and R_{13} are as defined and X_1 and/or X_2 are sulfur (Reaction Scheme 1), or when X_2 is oxygen,

ab) alkylation of compounds of formula IW_{1a}

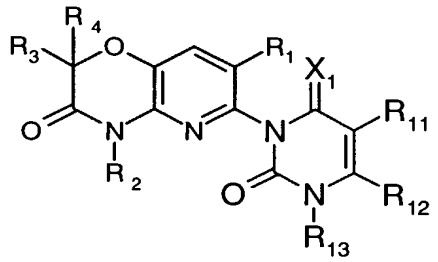


(IW$_{1a}$),

wherein R_1, R_2, R_3, R_4, R_{11}, R_{12} and X_1 are as defined for formula I and R_{13} is hydrogen, in the presence of a base, for example an alkali metal carbonate, e.g. potassium carbonate or sodium hydrogen carbonate, using an alkylating reagent of formula IX

R_{13}-L_1 (IX),

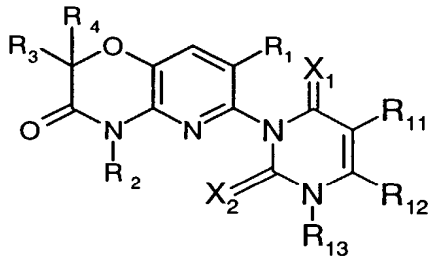
wherein R_{13} is as defined for formula I with the exception of R_{13} as hydrogen and amino, and L_1 is a leaving group, for example halogen, especially chlorine, bromine or iodine, or a sulfonate, especially mesyloxy or tosyloxy, to form the compound of formula IW_{1a}



(IW_{1a}) ,

wherein R_1, R_2, R_3, R_4, R_{11}, R_{12}, R_{13} and X_1 are as defined, (Reaction Scheme 1), or

ac) alkylation of compounds of formula IW_1

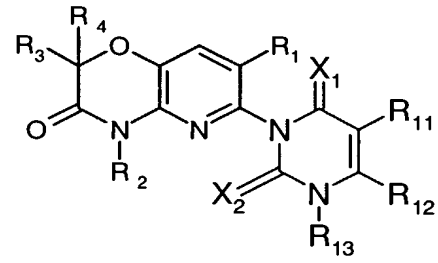


(IW_1) ,

wherein R_1, R_3, R_4, R_{11}, R_{12}, R_{13}, X_1 and X_2 are as defined for formula I with the exception of R_{13} as amino, and R_2 is hydrogen, in the presence of a base, for example an alkali metal carbonate, especially potassium carbonate, and a catalyst, for example 18-crown-6 or potassium iodide, using an alkylating reagent of formula IV

R_2-L_2 (IV),

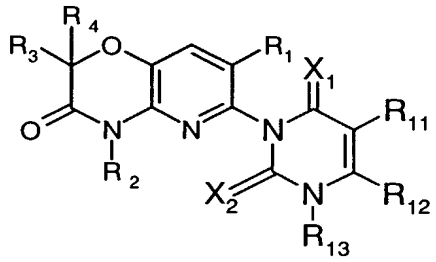
wherein R_2 is as defined for formula I with the exception of R_2 as hydrogen, and L_2 is a leaving group, for example halogen, especially chlorine, bromine or iodine, or a sulfonate, especially mesyloxy or tosyloxy, to form the compound of formula IW_1



(IW_1) ,

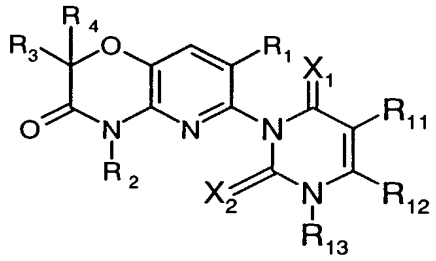
wherein R_1, R_2, R_3, R_4, R_{11}, R_{12}, R_{13}, X_1 and X_2 are as defined (Reaction Scheme 1), with the proviso that, when X_2 in the compound of formula IW_1 is sulfur, R_{13} must be other than hydrogen (S-alkylation), or

ad) amination of compounds of formula IW_1



(IW_1) ,

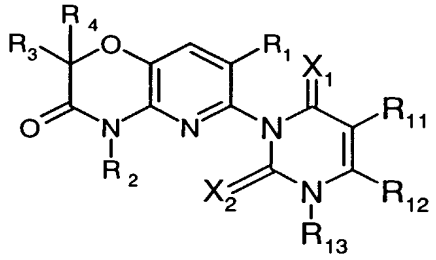
wherein R_1, R_2, R_3, R_4, R_{11}, R_{12}, X_1 and X_2 are as defined for formula I and R_{13} is hydrogen, using an electrophilic aminating reagent, for example 1-aminooxy-2,4-dinitrobenzene, in analogous manner to that described, for example, in WO 96/36614, to form the compound of formula IW_1



(IW_1) ,

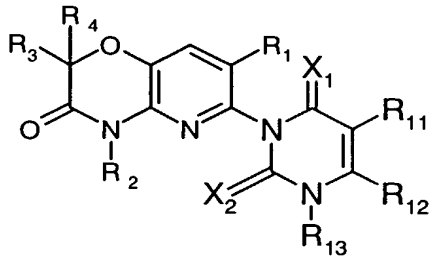
wherein R_1, R_2, R_3, R_4, R_{11}, R_{12}, X_1 and X_2 are as defined and R_{13} is amino (Reaction Scheme 1), or

ae) halogenation of compounds of formula IW_1



(IW_1) ,

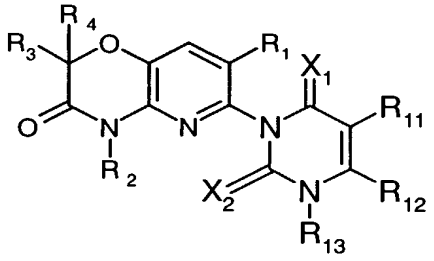
wherein R_2, R_3, R_4, R_{12}, R_{13}, X_1 and X_2 are as defined for formula I and R_1 and/or R_{11} are hydrogen, using a halogenating reagent, for example chlorine, bromine or iodine, to form the compound of formula IW_1



(IW_1) ,

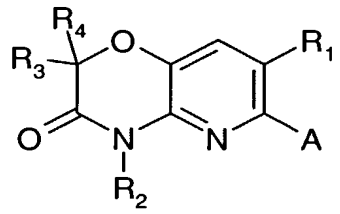
wherein R_2, R_3, R_4, R_{12}, R_{13}, X_1 and X_2 are as defined and R_1 and/or R_{11} are halogen (Reaction Scheme 1), or

af) fluorination of compounds of formula IW_1



(IW_1),

wherein R_2, R_3, R_4, R_{12}, R_{13}, X_1 and X_2 are as defined for formula I and R_1 and/or R_{11} are hydrogen, using an electrophilic fluorinating reagent, for example $FN(SO_2CF_3)_2$ or Selectfluor™ (= 1-chloromethyl-4-fluoro-1,4-diazabicyclo[2.2.2]octane bis(tetrafluoroborate); Manufacturer: Air Products European Technology Group, England), preferably after activation by means of a metallation reaction, for example using n-butyllithium, sec-butyllithium or lithium diisopropylamide (LDA), and advantageously with the aid of an ortho-directing group, for example a uracil radical in a compound of formula IW_1 or a group A in a compound of formula II

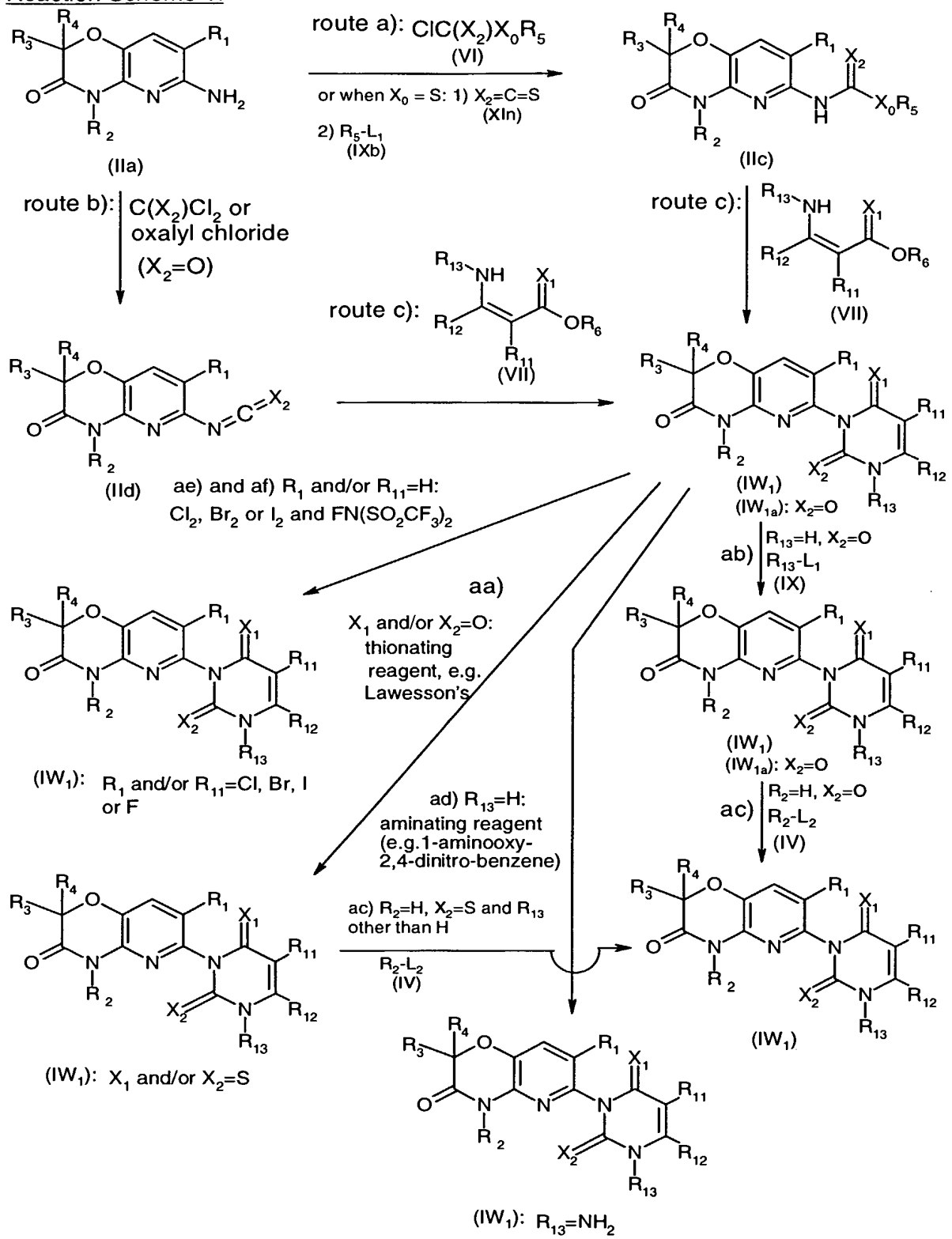


(II),

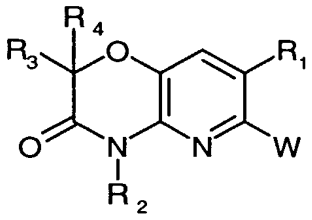
wherein R_2, R_3 and R_4 are as defined for formula I, R_1 is hydrogen, and A is, for example, a group $-NHC(X_2)R_5$ or $-NHC(X_2)X_0R_5$, wherein X_2 is oxygen or sulfur, X_0 is oxygen, sulfur or amino, and R_5 is C_1-C_6alkyl or phenyl, to form the compound of formula IW_1 wherein R_2, R_3, R_4, R_{12}, R_{13}, X_1 and X_2 are as defined and R_1 and/or R_{11} are fluorine, or to form the compound of formula II wherein R_2, R_3, R_4 and A are as defined and R_1 is fluorine (Reaction Scheme 1).

The fluorination may advantageously be carried out in an organic solvent, for example a cyclic ether, e.g. tetrahydrofuran, in the presence of an auxiliary base, for example tetramethylethylenediamine, and a further polar, aprotic solvent.

Reaction Scheme 1:

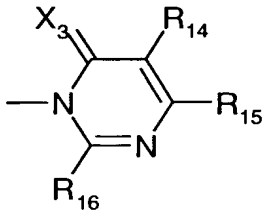


The process according to the invention for the preparation of compounds of formula I is carried out according to variant b) and Reaction Scheme 1b) and comprises, for the preparation of those compounds of formula I



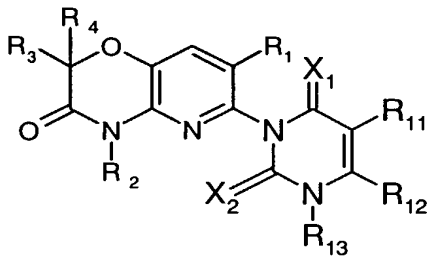
(I)

wherein R_1, R_2, R_3 and R_4 are as defined for formula I and W is a group W_2



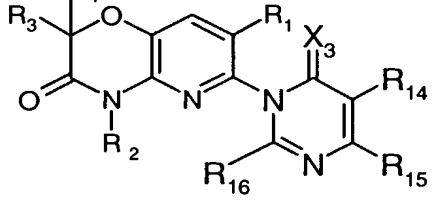
(W_2),

wherein R_{14}, R_{15} and X_3 are as defined for formula I and R_{16} is hydrogen, C_1-C_3alkyl, C_1-C_3haloalkyl, halogen, C_1-C_3alkoxy, C_1-C_3haloalkoxy, mercapto, C_1-C_3alkylthio, C_1-C_3alkylsulfinyl, C_1-C_3alkylsulfonyl, allylthio, propargylthio, amino, C_1-C_3alkylamino, di(C_1-C_3alkyl)amino, allylamino, propargylamino or cyano, treating a compound of formula IW_1



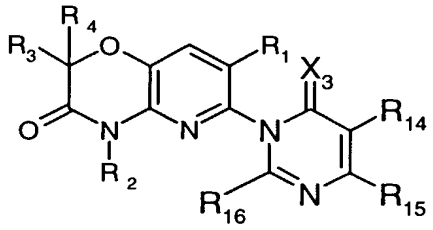
(IW_1),

wherein R_1, R_2, R_3, R_4, R_{11}, R_{12}, X_1 and X_2 are as defined for formula I and R_{13} is hydrogen, either, according to route f) in Reaction Scheme 2, with an alkylating reagent, for example R_{13}-L_1 of formula IX, wherein R_{13} is C_1-C_3alkyl, C_1-C_3haloalkyl, allyl or propargyl, and L_1 is a leaving group, for example halogen, especially chlorine, bromine or iodine, or a sulfonate, especially mesyloxy, or with a dialkyl sulfate of formula $(R_2O)_2SO_2$, wherein R_2 is as defined for formula I with the exception of R_2 as hydrogen, or with a Meerwein's salt ($R_3O{\bullet}BF_4$), wherein R is preferably methyl or ethyl, or a freonising reagent, for example CHF_2Cl or $BrCH_2F$, and thereby effecting direct conversion into the compound of formula IW_2



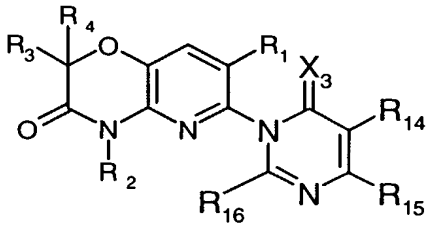
(IW_2),

wherein R_1, R_2, R_3 and R_4 are as defined, R_{14}, R_{15} and X_3 are as defined for R_{11}, R_{12} and X_1, respectively, and R_{16} is C_1-C_3alkoxy, C_1-C_3haloalkoxy, C_1-C_3alkylthio, allylthio or propargylthio, or, according to route d) in Reaction Scheme 2, first of all obtaining, using a halogenating reagent, for example phosphorus oxychloride, the compound of formula IW_2



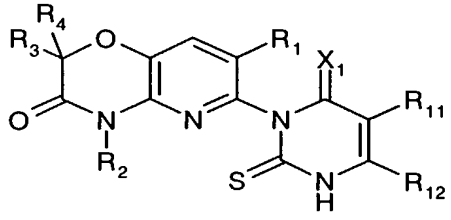
(IW_2),

wherein R_1, R_2, R_3 and R_4 are as defined, R_{14}, R_{15} and X_3 are as defined for R_{11}, R_{12} and X_1, respectively, and R_{16} is halogen, especially chlorine, and then converting that compound *via* a nucleophilic substitution reaction, for example with a C_1-C_3alcoholate, a C_1-C_3alkylthiolate or an alkali metal cyanide, into the compound of formula IW_2



(IW_2),

wherein R_1, R_2, R_3, R_4, R_{14}, R_{15} and X_3 are as defined and R_{16} is C_1-C_3alkoxy, C_1-C_3alkylthio or cyano, or, when X_2 in the compound of formula IW_1 is oxygen, first of all converting that compound, according to route e) in Reaction Scheme 2, using a thionating reagent, for example phosphorus pentasulfide (P_2S_5), into the compound of formula IW_{1g}



(IW_{1g}),

wherein R_1, R_2, R_3, R_4, R_{11}, R_{12} and X_1 are as defined, and then treating that compound with an alkylating reagent of formula

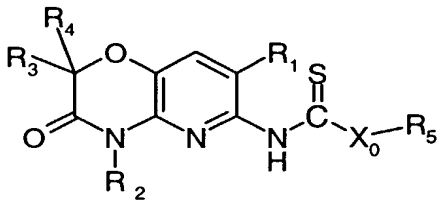
$$R_{13}\text{-}L_1 \qquad (IX),$$

wherein R_{13} is C_1-C_3alkyl, C_1-C_3haloalkyl, allyl or propargyl, and L_1 is a leaving group, for example halogen, especially chlorine, bromine or iodine, or sulfonate, especially mesyloxy or tosyloxy, for example a C_1-C_3alkyl halide, especially methyl iodide, or C_1-C_3alkyl sulfate, especially dimethyl sulfate, and optionally of formula IV

R_2-L_2 (IV),

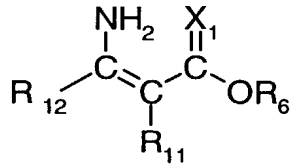
wherein R_2 is as defined for formula I with the exception of R_2 as hydrogen, and L_2 is a leaving group, for example halogen, especially chlorine, bromine or iodine, or sulfonate, especially mesyloxy or tosyloxy, to thereby yield the compound of formula IW_2 wherein R_1 to R_4, R_{14}, R_{15} and X_3 are as defined and R_{16} is C_1-C_3alkylthio, C_1-C_3haloalkylthio, allylthio or propargylthio (route f) in Reaction Scheme 2,

or, for the preparation of compounds of formula IW_{1g} according to route ka) in Reaction Scheme 2, reacting a compound of formula IIc_4



(IIc_4),

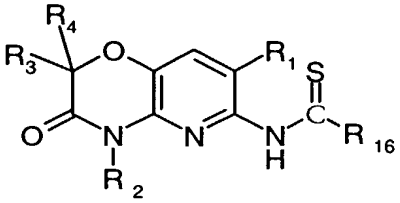
wherein R_1, R_2, R_3 and R_4 are as defined hereinbefore, X_0 is oxygen, sulfur or amino, and R_5 is C_1-C_4alkyl or phenyl, with an enamine derivative of formula VIIa



(VIIa),

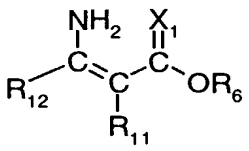
wherein R_{11}, R_{12} and X_1 are as defined and R_6 is C_1-C_4alkyl,

or, according to route kb) in Reaction Scheme 2, reacting a compound of formula IIc_6



(IIc_6),

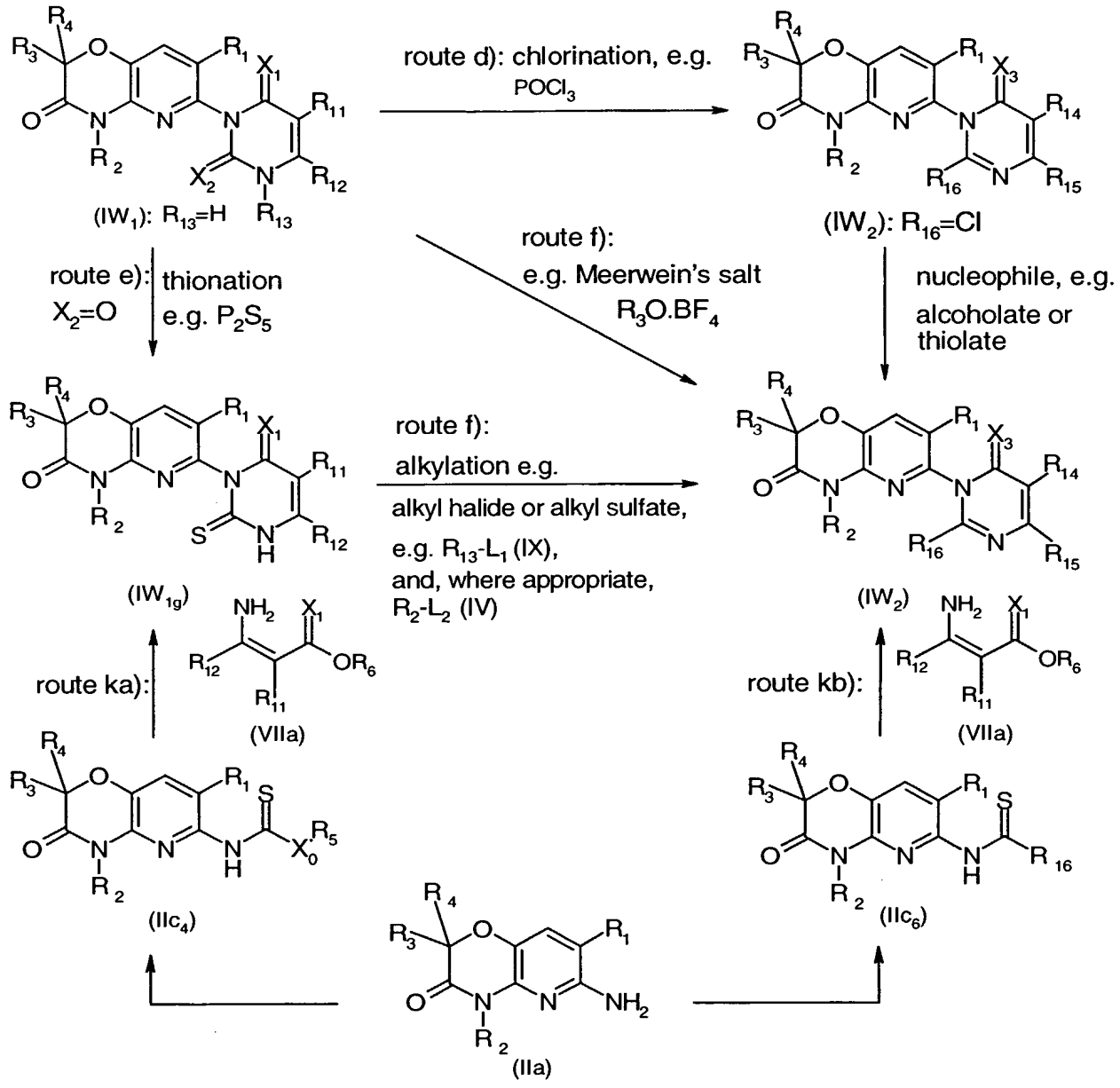
wherein R_1, R_2, R_3 and R_4 are as defined and R_{16} is C_1-C_3alkyl or C_1-C_3haloalkyl, with an enamine derivative of formula VIIa



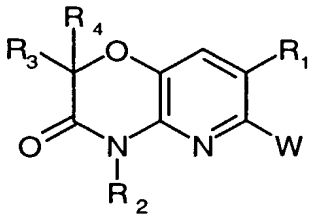
(VIIa),

wherein R_{11}, R_{12} and X_1 are as defined and R_6 is C_1-C_4alkyl, to yield the compounds of formula IW_2, wherein R_{14}, R_{15} and X_3 are as defined for R_{11}, R_{12} and X_1, respectively, in compounds of formulae VIIa and IW_1, and R_{16} is as defined.

Reaction Scheme 2:

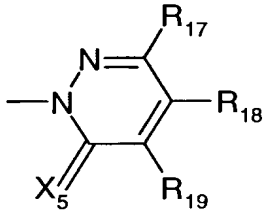


The process according to the invention for the preparation of compounds of formula I according to variant b) and Reaction Scheme 1b) comprises, for the preparation of those compounds of formula I



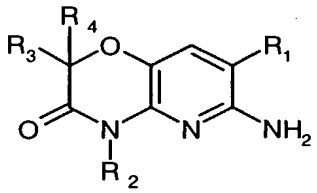
(I)

wherein R_1, R_2, R_3 and R_4 are as defined for formula I and W is a group W_3



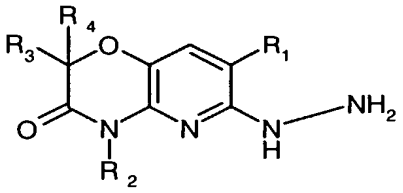
(W_3),

wherein R_{17}, R_{18}, R_{19} and X_5 are as defined for formula I, first of all converting a compound of formula IIa



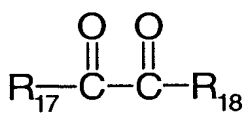
(IIa) ,

wherein R_1, R_2, R_3 and R_4 are as defined for formula I, under standard diazotisation conditions, e.g. using HNO_3/H_2SO_4, and with reduction of the diazonium salt, as described, for example, in 'Methoden der Organischen Chemie (Houben-Weyl)', volume X/2 (Stickstoffverbindungen), Georg Thieme Verlag, Stuttgart, 1967, pages 180 ff., into the hydrazine derivative of formula IIe

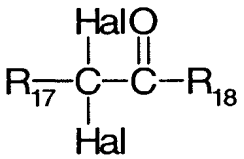


(IIe)

and then condensing that compound with the reagent of formula XIa or XIb

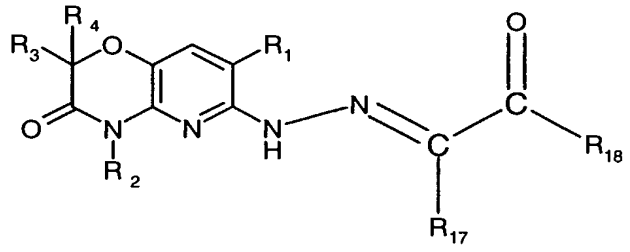


(XIa) or



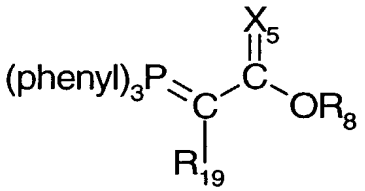
(XIb),

wherein R_{17} and R_{18} are as defined for formula I and Hal is halogen, especially chlorine or bromine, to form the hydrazone derivative of formula IIf



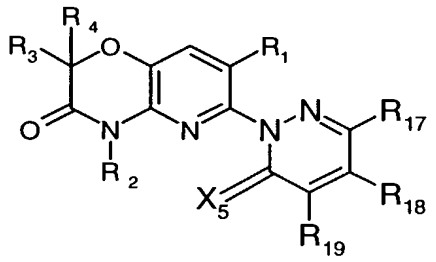
(IIf) ,

the substituents R_1, R_2, R_3, R_4, R_{17} and R_{18} in the compounds of formulae IIe and IIf being defined as indicated, and then condensing and cyclising (as illustrated in Reaction Scheme 3) the compound of formula IIf with the Wittig reagent of formula VIII



(VIII),

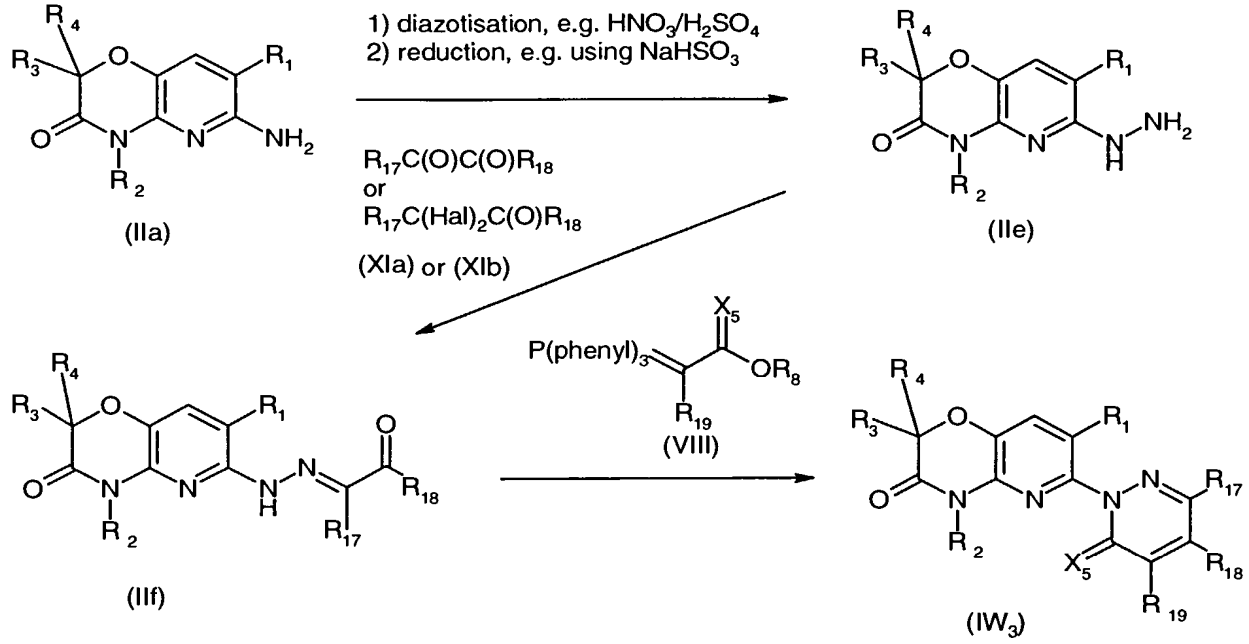
wherein R_{19} and X_5 are as defined for formula I and R_8 is C_1-C_4alkyl, in the presence of from 0.01 to 1.5 equivalents of a suitable base, for example an alkali metal hydride or alcoholate, e.g. sodium hydride or potassium tert-butanolate, in an inert solvent, for example an ether, e.g. THF, an aromatic hydrocarbon, e.g. toluene or one of the xylene isomers, or an amide, e.g. NMP, to form the compound of formula IW_3



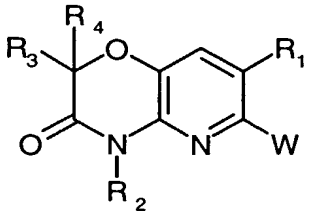
(IW_3),

wherein R_1, R_2, R_3, R_4, R_{17}, R_{18}, R_{19} and X_5 are as defined, and, optionally, further functionalising that compound according to the definitions of R_1, R_2, R_{18} and X_5 in analogous manner to that described under aa), ac) or ae).

Reaction Scheme 3:

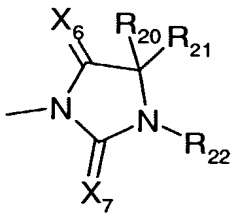


The process according to the invention for the preparation of compounds of formula I according to variant b) and Reaction Scheme 1b is carried out analogously to known processes, as described, for example, in WO 99/52893, EP-A-0 272 594, EP-A-0 493 323, DE-A-3 643 748, WO 95/23509, US-A-5 665 681 and US-A-5 661 109, and comprises, for the preparation of those compounds of formula I



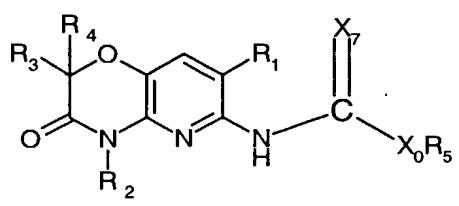
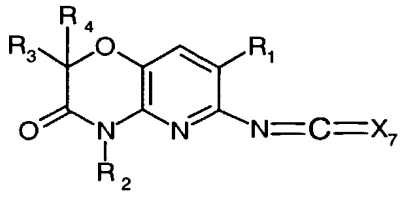
(I)

wherein R_1, R_2, R_3 and R_4 are as defined for formula I and W is a group W_4

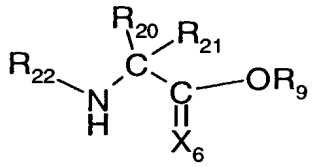


(W_4),

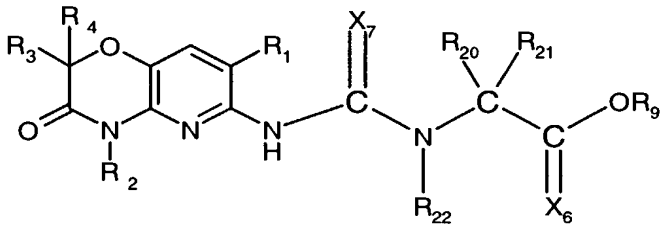
wherein R_{20}, R_{21}, R_{22} and X_7 are as defined for formula I, reacting a compound of formula IIc_1 or IId_1


(IIc$_1$) or

(IId$_1$),

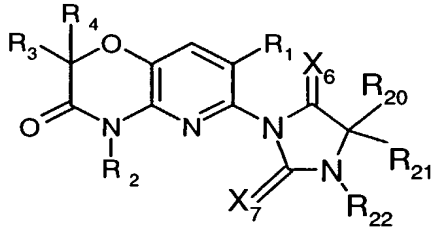
wherein R_1, R_2, R_3, R_4 and X_7 are as defined for formula I, X_0 is oxygen, sulfur or amino, and R_5 is C_1-C_4alkyl, with an amino acid ester of formula XIII


(XIII),

wherein R_{20}, R_{21}, R_{22} and X_6 are as defined for formula I and R_9 is C_1-C_4alkyl, to form the compound of formula IIg


(IIg),

wherein R_1, R_2, R_3, R_4, R_9, R_{20}, R_{21}, R_{22}, X_6 and X_7 are as defined, and then cyclising (Reaction Scheme 4) the resulting compound to form the compound of formula IW$_4$


(IW$_4$)

and, optionally, further functionalising that compound according to the definitions of R_1, R_2, R_{20}, R_{21}, R_{22}, X_6 and X_7 in analogous manner to that described under aa), ac) or ae).
For example, the compound of formula IW$_4$ wherein R_{22} is hydrogen and X_7 is oxygen can, in analogous manner to that described under ac), be further reacted with an alkylating reagent of formula X

$$R_{22}\text{-}L_5 \qquad (X),$$

wherein R_{22} is C_1-C_3alkyl and L_5 is a leaving group, for example halogen, especially chlorine, bromine or iodine, or a sulfonate, especially mesyloxy or tosyloxy, in the presence

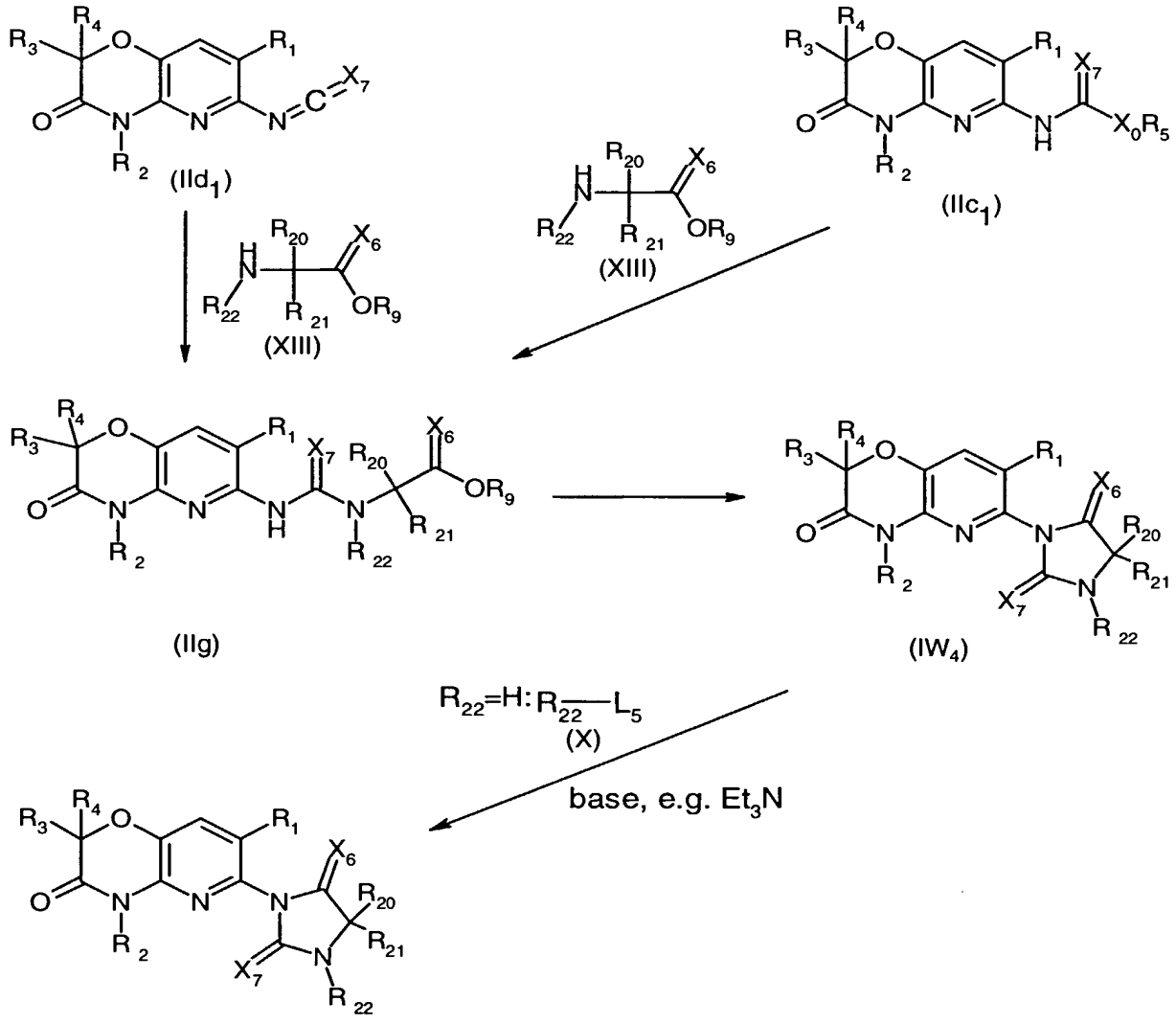
of a suitable base, for example a trialkylamine or an alkali metal carbonate, to form the compound of formula IW_4 wherein R_{22} is C_1-C_3alkyl.

Moreover, for example, the compound of formula IW_4 wherein R_{22} and R_{20} or R_{22} and R_{21} together form a C_3-C_5alkylene bridge which is, for example,

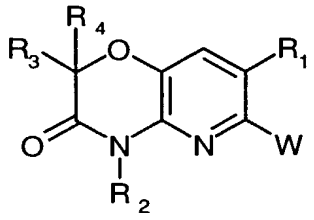
1) interrupted by -C(O)- or substituted by hydroxy, can readily be converted, by standard methods, for example using the reagent DAST (diethylaminosulfur trifluoride) or Deoxyfluor™ (= bis(2-methoxymethyl)aminosulfur trifluoride), into the corresponding derivatives substituted once or twice by fluorine (Example 19), or

2) interrupted by sulfur, can readily be converted, using a suitable oxidising agent, for example sodium periodate ($NaIO_4$), into the corresponding -S(O)- or -$S(O)_2$- derivative.

Reaction Scheme 4:

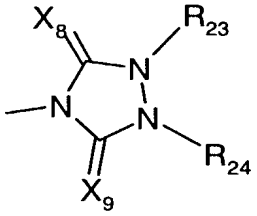


The process according to the invention for the preparation of compounds of formula I according to variant b) and Reaction Scheme 1b is carried out analogously to known processes, as described, for example, in WO 99/52893, EP-A-0 210 137, DE-A-2 526 358, EP-A-0 075 267 and EP-A-0 370 955, and comprises, for the preparation of those compounds of formula I



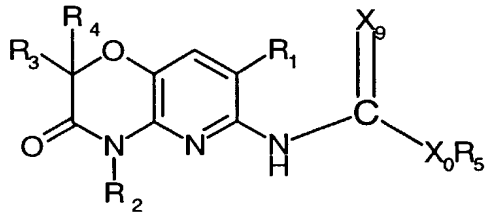
(I)

wherein R_1, R_2, R_3 and R_4 are as defined for formula I and W is a group W_5

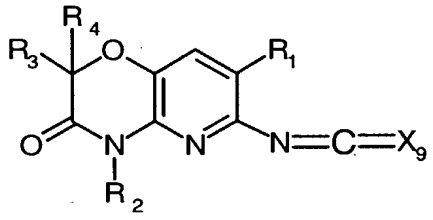


(W_5),

wherein R_{23}, R_{24}, X_8 and X_9 are as defined for formula I, either, according to Reaction Scheme 5, reacting a compound of formula IIc_2 or IId_2

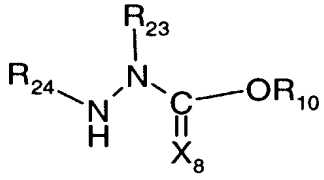


(IIc_2) or



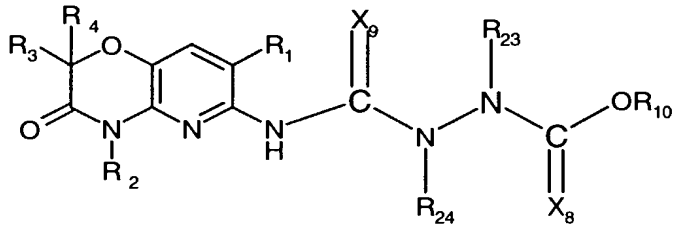
(IId_2),

wherein R_1, R_2, R_3, R_4 and X_9 are as defined for formula I, X_0 is oxygen, sulfur or amino, and R_5 is C_1-C_4alkyl, with a hydrazide ester of formula XIV



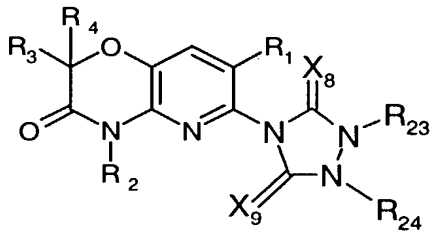
(XIV),

wherein R_{23}, R_{24} and X_8 are as defined for formula I and R_{10} is C_1-C_4alkyl, in the presence of a base, for example a trialkylamine, and a suitable solvent, for example a chlorinated hydrocarbon, e.g. chlorobenzene, or an amide, e.g. DMF or NMP, to thereby yield the compound of formula IIh



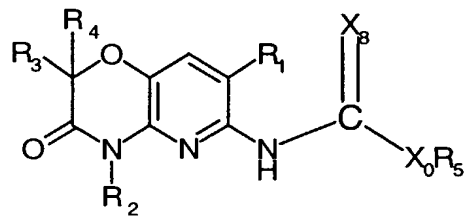
(IIh),

wherein R_1, R_2, R_3, R_4, R_{10}, R_{23}, R_{24}, X_8 and X_9 are as defined, and then cyclising that compound to form the compound of formula IW_5

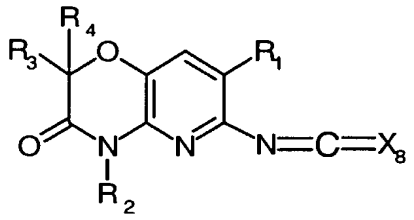


(IW_5) ,

or, according to Reaction Scheme 5a, reacting a compound of formula IIc_5 or IId_5



(IIc_5) or

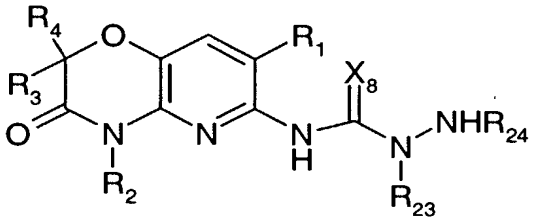


(IId_5),

wherein R_1, R_2, R_3, R_4, R_5, X_0 and X_8 are as defined, with a hydrazine of formula XXXVa

$$R_{24}NHNHR_{23} \qquad \text{(XXXVa)},$$

wherein R_{23} and R_{24} are as defined, to form the compound of formula IIp



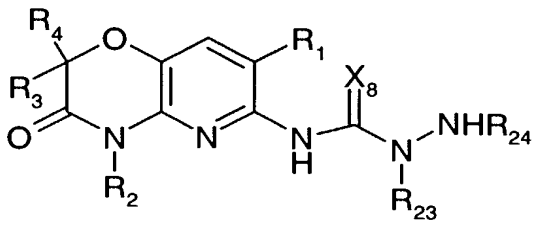
(IIp)

and cyclising that compound, according to route r) in Reaction Scheme 5a, with phosgene, thiophosgene or a chloroformate of formula VIa

$$ClC(X_9)OR_9 \qquad \text{(VIa)}$$

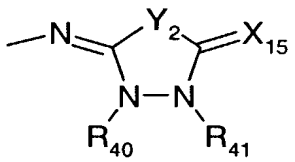
wherein X_9 is as defined and R_9 is C_1-C_4alkyl.

According to Reaction Scheme 5a, route s), starting from the compounds of formula IIp



(IIp)

wherein R_1, R_2, R_3 and R_4 are as defined for formula I with the proviso that X_8, R_{23} and R_{24} are as defined for Y_2, R_{40} and R_{41}, respectively, the compounds of formula I wherein W is a group W_{12}



(W_{12})

and R_{40}, R_{41}, Y_2 and X_{15} are as defined for formula I, can be obtained by reaction with phosgene, thiophosgene or a chloroformate of formula VIb

$$ClC(X_{15})OR_9 \qquad \text{(VIb)},$$

wherein X_{15} is as defined and R_9 is C_1-C_4alkyl. For example, the compounds of formula IW_{12} can be obtained by reacting compounds of formula IIp with phosgene in an aromatic hydrocarbon, e.g. toluene, and preferably in an additional solvent, for example an ether, e.g. tetrahydrofuran, and in the presence of a base as acid-binding agent, at temperatures of from 5° to 20°C.

The compound of formula IW_5 may, optionally, be further functionalised according to the definitions of R_1, R_2, R_{23}, R_{24}, X_8 and X_9 in analogous manner to that described under aa), ac) or ae).

For example, the compound of formula IW_5 wherein R_{23} and/or R_{24} are hydrogen can be further reacted, in analogous manner to that described under ac), with an alkylating reagent of formula XVa and/or XVb

$$R_{23}\text{-}L_3 \qquad \text{(XVa) and/or} \quad R_{24}\text{-}L_4 \qquad \text{(XVb)},$$

wherein R_{23} and R_{24} are as defined for formula I with the exception of R_{23} and R_{24} as hydrogen, and L_3 and L_4 are each a leaving group, for example halogen, especially chlorine, bromine or iodine, or a sulfonate, especially mesyloxy or tosyloxy, in the presence of a suitable base to form the compound of formula IW_5 wherein R_{23} and/or R_{24} are C_1-C_3alkyl or C_1-C_3haloalkyl. Optionally, the compound of formula IW_5 wherein R_2 is hydrogen, and R_{23} and R_{24} are other than hydrogen can be alkylated, in the presence of a base, for example

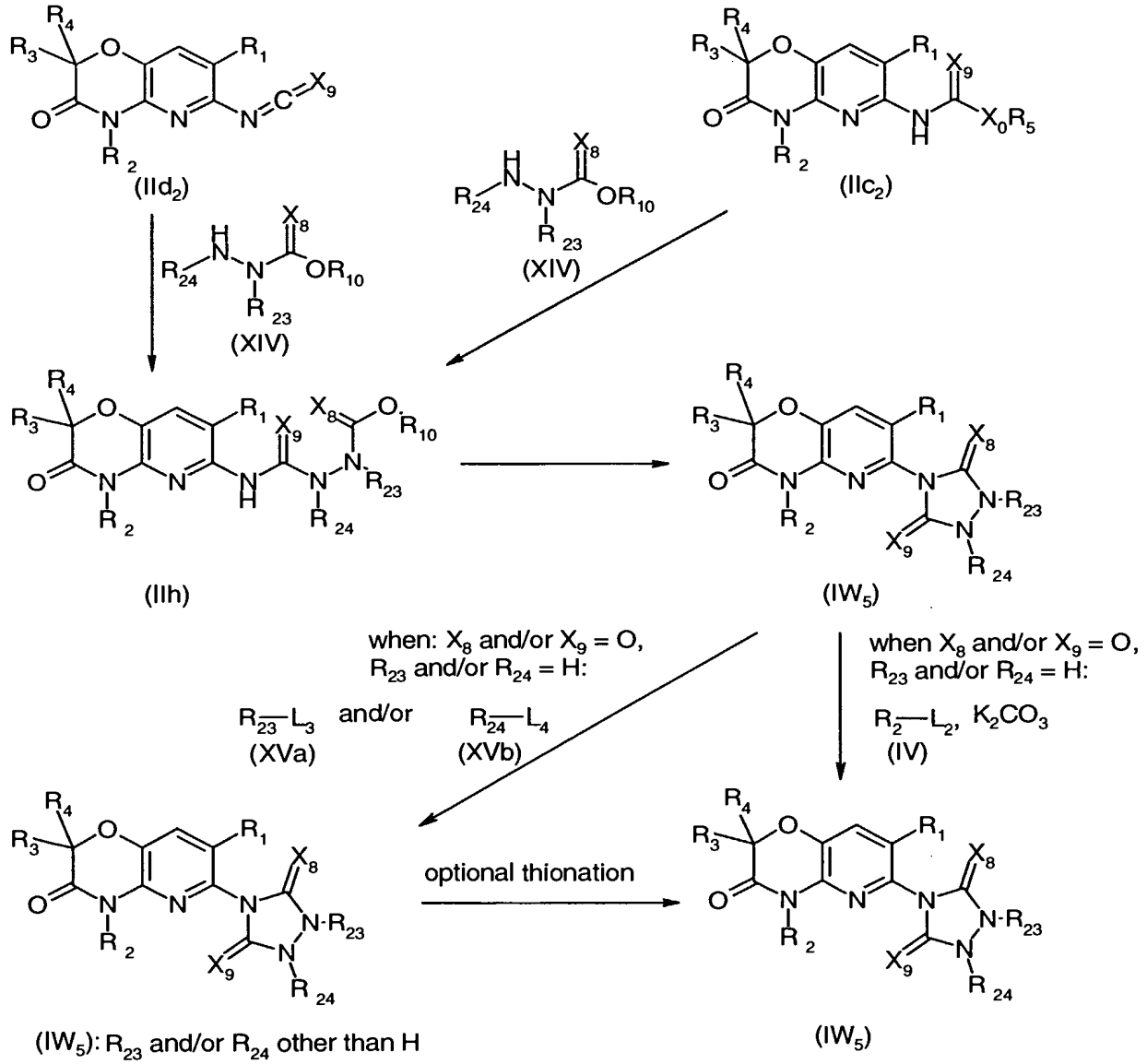
an alkali metal carbonate, e.g. potassium carbonate, as acid-binding agent, with the reagent of formula IV

$$R_2\text{-}L_2 \qquad (IV),$$

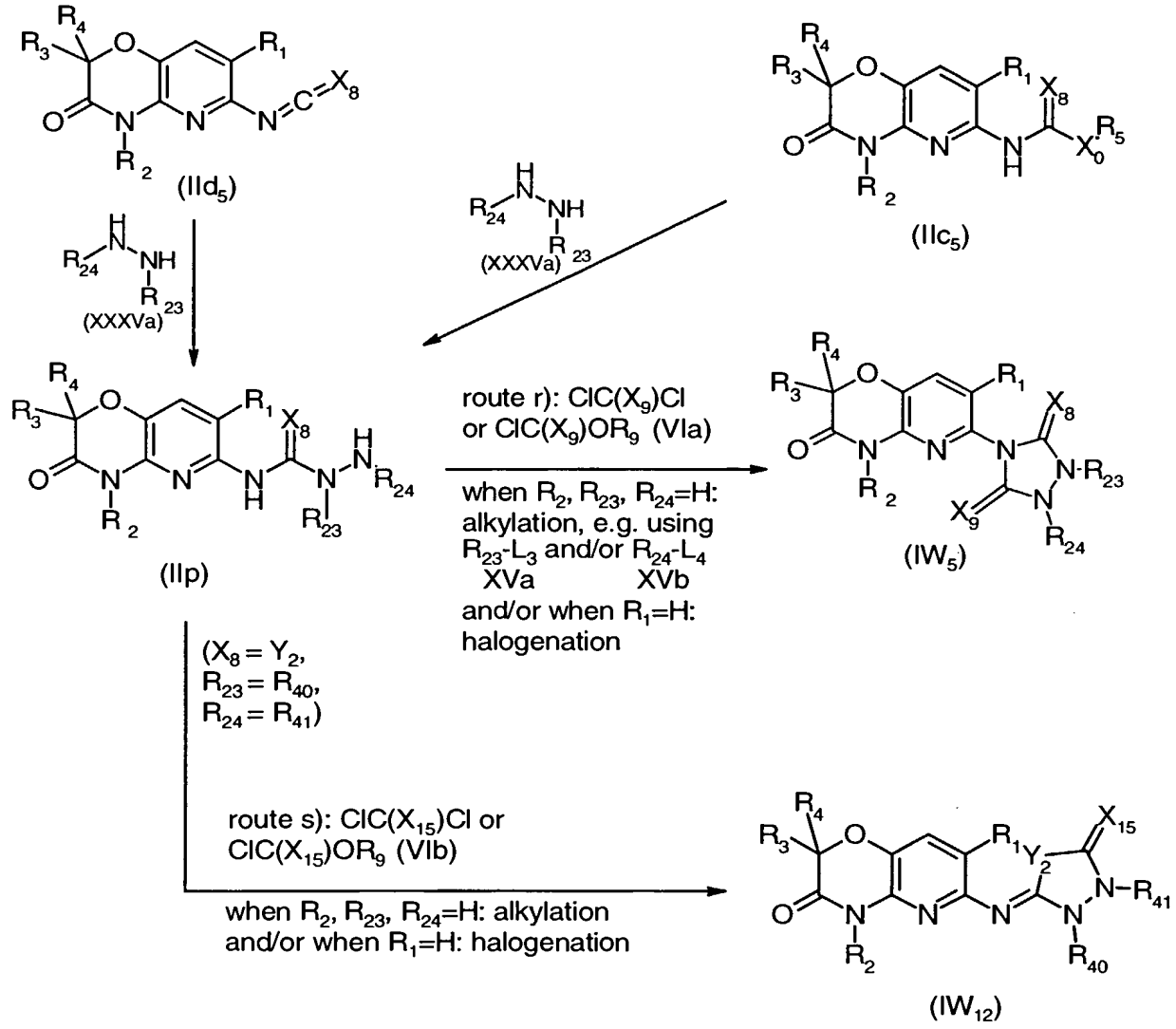
wherein R_2 is as defined for formula I with the exception of R_2 as hydrogen, and L_2 is a leaving group, for example halogen, e.g. chlorine, bromine or iodine, or sulfonate, e.g. mesyloxy or tosyloxy.

Likewise, the compound of formula IW_{12} may be further functionalised (R_1, R_2, R_{23}, R_{24} or R_{40} and R_{41}, and X_{15}) in Reaction Scheme 5a according to the standard methods described under aa), ac) and ae). That possibility is also illustrated in Reaction Schemes 5 and 5a.

Reaction Scheme 5:



Reaction Scheme 5a:

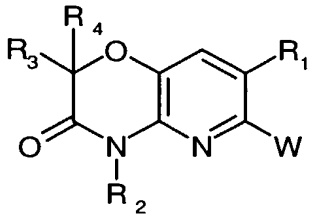


It is also possible to prepare the compounds of formula I wherein W is a group W_6, W_7, W_8, W_9 and W_{12} analogously to the process according to the invention described above according to variant b) and as illustrated in Reaction Scheme 1b. Such processes are described, for example, in WO 99/52893.

Furthermore, WO 00/15633 describes general processes according to variant b) above, according to which processes it is also possible to prepare the compounds of formula I wherein W is a group W_1, W_2, W_3, W_4, W_5, W_6, W_7, W_8, W_9, W_{10}, W_{11}, W_{13}, W_{15}, W_{19} or W_{20}.

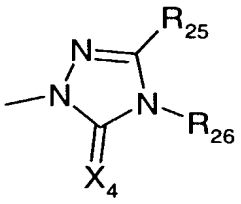
The process of the invention according to variant b) for the preparation of compounds of formula I is carried out analogously to known processes, as described, for example, in J. Org. Chem. 56, 5643 (1991), J. Heterocycl. Chem. 27, 2017 (1990), DE-OS-3 917 469,

WO 94/22828, WO 88/09617 and US-A-5 449 784, and comprises, for the preparation of those compounds of formula I



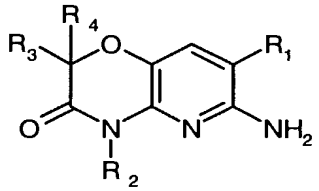
(I)

wherein R_1, R_2, R_3 and R_4 are as defined for formula I and W is a group W_6



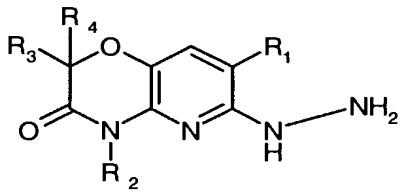
(W_6),

wherein R_{25}, R_{26} and X_4 are as defined for formula I, first of all converting a compound of formula IIa



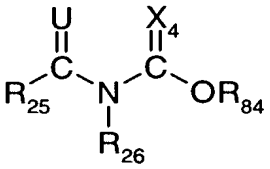
(IIa) ,

wherein R_1, R_2, R_3 and R_4 are as defined for formula I, under diazotisation conditions and with reduction of the diazonium salt, as described, for example, in 'Methoden der Organischen Chemie (Houben-Weyl)', volume X/2 (Stickstoffverbindungen), Georg Thieme Verlag, Stuttgart, 1967, pages 180 ff., into the hydrazine derivative of formula IIe



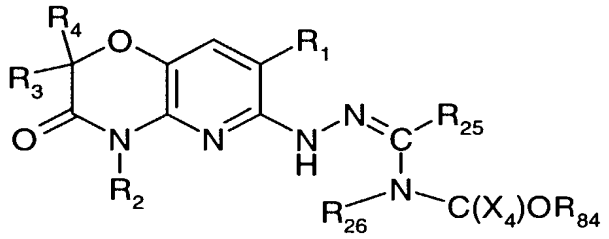
(IIe)

and then, according to route g) in Reaction Scheme 6, condensing that compound with the reagent of formula XIc



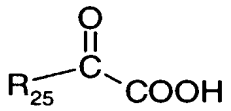
(XIc),

wherein R_{25}, R_{26} and X_4 are as defined, U is oxygen, sulfur or imino, and R_{84} is C_1-C_4alkyl, optionally in the presence of a base, for example an alcoholate, e.g. sodium ethanolate or potassium tert-butanolate, or an amine, e.g. triethylamine or pyridine, or a carbonate, e.g. potassium carbonate, in a suitable solvent, for example an alcohol, e.g. ethanol, an amide, e.g. DMF or NMP, or pyridine, at temperatures from 20° to the boiling point of the solvent used, to yield the hydrazone derivative of formula IIj



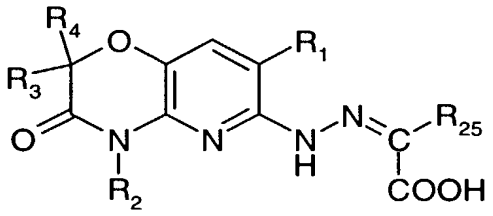
(IIj)

and then cyclising that compound either with base catalysis, for example using an alcoholate, e.g. sodium ethanolate, or preferably with acid catalysis, for example using a carboxylic acid, e.g. acetic acid, or a sulfonic acid, e.g. p-toluenesulfonic acid, in a suitable solvent as mentioned above or also, for example, in a carboxylic acid, e.g. acetic acid, or, according to route h) in Reaction Scheme 6, condensing the compound of formula IIe with the reagent of formula XId



(XId),

wherein R_{25} is as defined, with acid catalysis, for example using an C_1-C_4alkylcarboxylic acid, e.g. propionic acid, a mineral acid, e.g. hydrochloric or sulfuric acid, or a sulfonic acid, e.g. p-toluenesulfonic acid, to yield the hydrazone derivative of formula IIw

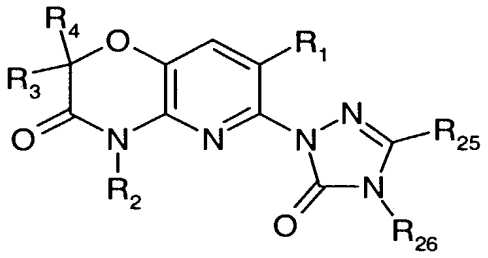


(IIw)

and subsequently cyclising that compound in a solvent, for example a halogenated hydrocarbon, e.g. chlorobenzene, or an amide, e.g. NMP, under basic conditions, for example in the presence of an alkali metal hydroxide or alcoholate, e.g. potassium hydroxide or potassium tert-butanolate, with an azide of formula XXXIX

$(R_{60}O)_2P(O)N_3$ (XXXIX),

wherein R_{60} is C_1-C_4alkyl, to form the compound of formula IW_{6a}



(IW$_{6a}$),

wherein R_1, R_2, R_3, R_4 and R_{25} are as defined and R_{26} is hydrogen, and then optionally converting into the compounds of formula IW$_6$ using the reagent of formula Xa

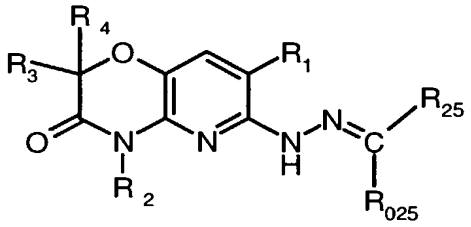
$$R_{26}\text{-}L_5 \qquad \text{(Xa)},$$

wherein R_{26} is C_1-C_4alkyl or C_1-C_4haloalkyl, e.g. methyl or bromodifluoromethyl, and L_5 is a leaving group, for example halogen, especially chlorine, bromine or iodine, or a sulfonate, especially mesyloxy or tosyloxy, in an inert organic solvent, for example a nitrile, e.g. acetonitrile, an amide, e.g. DMF or NMP, a chlorinated hydrocarbon, e.g. chloroform, an aromatic hydrocarbon, e.g. toluene or one of the xylene isomers, or in water, or in a two-phase system consisting of a water-immiscible solvent and water, in the presence of a phase-transfer catalyst, for example a quaternary ammonium salt, e.g. tetrabutylammonium bromide, and in the presence of a base, for example a hydroxide, e.g. an alkali metal hydroxide, or a carbonate, e.g. an alkali metal carbonate,

or, according to route i) in Reaction Scheme 6, condensing the compound of formula IIe with a compound of formula XIe

$$R_{25}C(O)R_{025} \qquad \text{(XIe)},$$

wherein R_{25} is C_1-C_4alkyl or C_1-C_4haloalkyl, and R_{025} is hydrogen, C_1-C_4alkyl, furyl or phenyl, in a suitable solvent, for example an aromatic hydrocarbon, e.g. one of the xylene isomers, a halogenated hydrocarbon, e.g. chlorobenzene, a ketone, e.g. methyl ethyl ketone, or an amide, e.g. NMP, and optionally with acid catalysis, e.g. using p-toluenesulfonic acid, and at elevated temperatures, advantageously with removal by azeotropic distillation of water of reaction that is formed, to form the hydrazone of formula IIe$_1$



(IIe$_1$),

wherein R_1, R_2, R_3, R_4, R_{25} and R_{025} are as defined, and then reacting that compound with an isocyanate or isothiocyanate of formula XIf

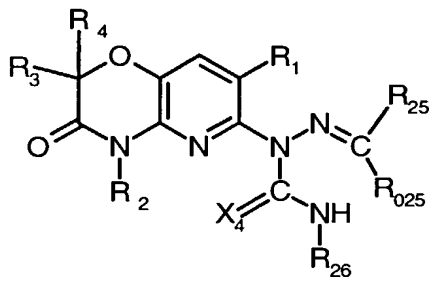
$R_{26}NCX_4$ (XIf)

wherein R_{26} is C_1-C_4alkyl or C_1-C_4haloalkyl and X_4 is oxygen or sulfur, or

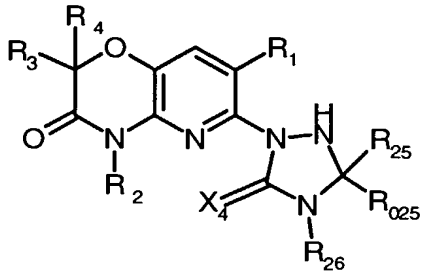
with an alkali metal cyanate or alkali metal thiocyanate of formula XIe_1

$X_4CN^- M^+$ (XIe_1),

wherein M^+ is an alkali metal ion and X_4 is as defined (e.g. Na^+ ^-OCN, K^+ ^-OCN, or K^+ ^-SCN), to thereby yield the compound of formula IIm_1 and/or IIm_2



(IIm_1) and/or



(IIm_2),

wherein R_1, R_2, R_3, R_4, R_2 and R_{025} are as defined. This reaction is advantageously carried out in a suitable solvent, for example a ketone, e.g. acetone, an alcohol, e.g. ethanol, a nitrile, e.g. acetonitrile, an amide, e.g. DMF or NMP, or in water, and optionally with addition of a base, for example an amine, e.g. triethylamine, or pyridine, or an acid, e.g. acetic acid or p-toluenesulfonic acid, at temperatures of from 20° to 180°C.

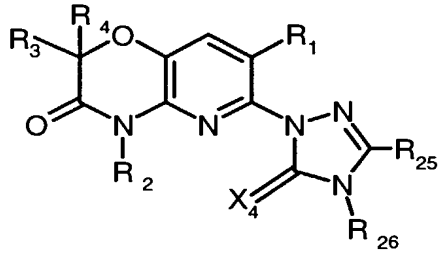
From compounds of formula IIm_1 and/or IIm_2, it is possible, according to route k) in Reaction Scheme 6, either 'in situ' or after their isolation, by reaction with a carboxylic acid of formula XIi or an activated form thereof of formula XIi_1

$R_{25}COOH$ (XIi) or $R_{25}C(O)$-L_{16} (XIi_1),

wherein R_{25} is C_1-C_4alkyl or C_1-C_4haloalkyl and L_{16} is a leaving group, for example halogen, e.g. chlorine (= acid chloride), or a carboxyl group -$OC(O)R_{25}$ (= anhydride), or with a corresponding ortho ester of formula XIi_2

$R_{25}C(OR_{61})_3$ (XIi_2),

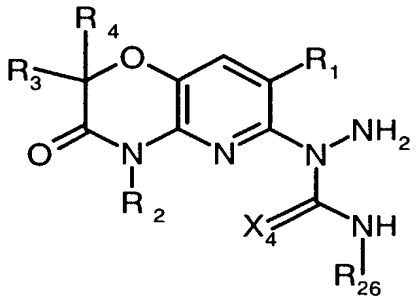
wherein R_{25} is as defined and R_{61} is methyl or ethyl, to yield the compounds of formula IW_6



(IW_6),

wherein R_1, R_2, R_3, R_4, R_{25}, R_{26} and X_4 are as defined.

According to route j) in Reaction Scheme 6, the compounds of formula IIm_1 and/or IIm_2 can first of all be hydrolysed to form the compound of formula IIm

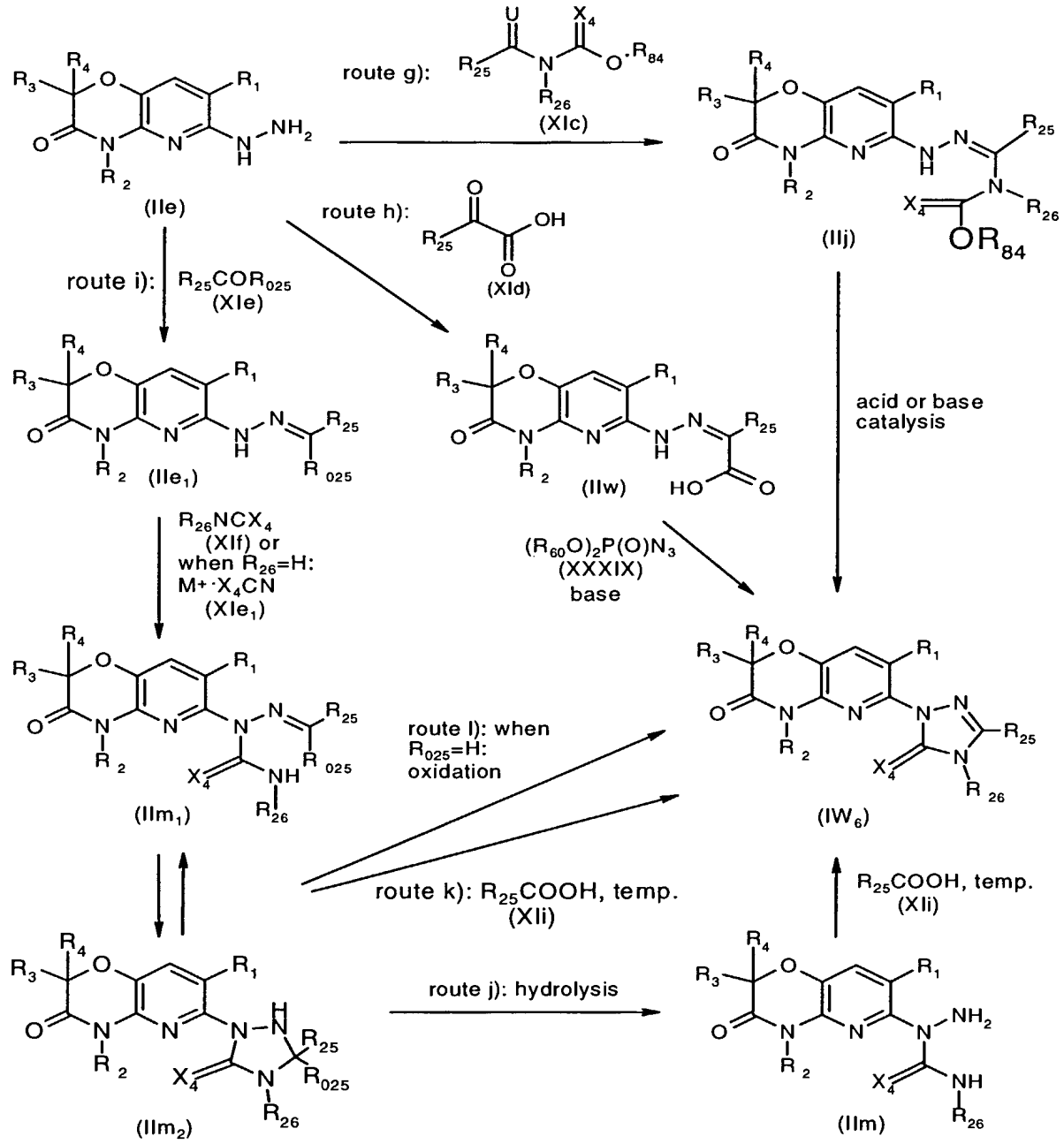


(IIm)

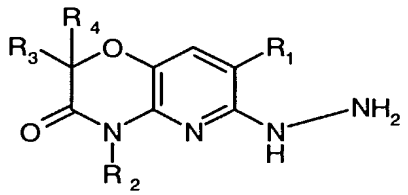
and then, in the presence of a carboxylic acid of formula XIi or an activated form thereof of formula XIi_1 or XIi_2, with heating, cyclised to form the compounds of formula IW_6. The reactions with the carboxylic acid of formula XIi are advantageously carried out without isolation of the compounds of formulae IIm_1 and/or IIm_2 or of formula IIm. The acid of formula XIi can be used in an equimolar amount and also as a solvent, for example acetic or propionic acid.

The compounds of formulae IIm_1 and/or IIm_2 wherein R_{025} is hydrogen can also, according to route I) in Reaction Scheme 6, be converted into the compounds of formula IW_6 in the presence of an oxidising agent, e.g. 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) or Javelle water, in a suitable solvent, for example a halogenated hydrocarbon, e.g. chlorobenzene, a carboxylic acid, e.g. acetic acid, an amide, e.g. NMP, or water, or a mixture thereof, at temperatures of from 0° to 130°C.
Reaction Scheme 6 illustrates those reactions, which are especially suitable for the preparation of compounds of formula IW_6 wherein R_{25} is hydrogen, C_1-C_4alkyl or C_1-C_4haloalkyl or wherein R_{26} and R_{25} together form a C_3-C_5alkylene bridge.
The compounds of formulae IW_{6a} and IW_6 wherein R_{26} and/or R_2 are hydrogen or R_1 is hydrogen and X_4 is oxygen may optionally be further functionalised, according to the definitions of R_1, R_2, R_{26} and X_4, as described above under ab) or ac) using an alkylating reagent, for example R_{26}-L_1 and R_2-L_2, or as described above under ae) or aa).

Reaction Scheme 6:



Starting from the compound of formula IIe



(IIe) ,

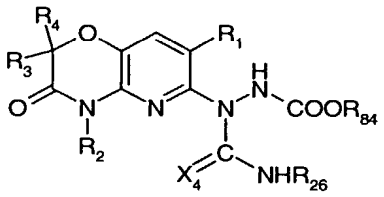
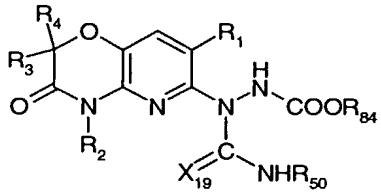
wherein R_1, R_2, R_3 and R_4 are as defined for formula I, it is also possible to prepare (according to variant b) and Reaction Scheme 1b) the compounds of formula I wherein W is a group W_6 (compounds of formula IW_6), W_{16} (compounds of formula IW_{16}) or W_{17} (compounds of formula IW_{17}) by reacting the compound of formula IIe first with a chloroformic acid ester of formula XXXIVa

$$ClCOOR_{84} \qquad (XXXIVa),$$

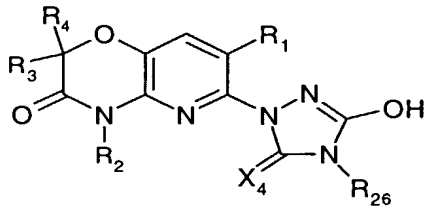
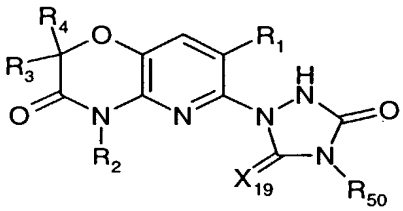
wherein R_{84} is C_1-C_4alkyl, and then with an isocyanate or isothiocyanate of formula XIf or XIg

$$R_{26}N=C=X_4 \quad (XIf) \qquad \text{or} \qquad R_{50}N=C=X_{19} \quad (XIg),$$

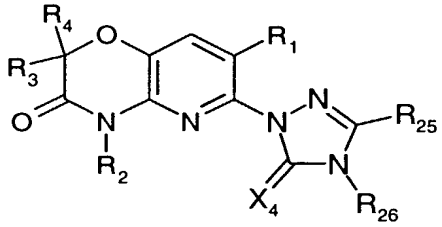
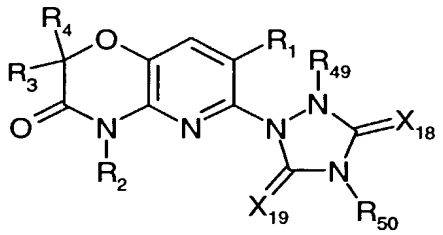
wherein R_{26} and R_{50} are C_1-C_4alkyl or C_1-C_4haloalkyl and X_4 and X_{19} are oxygen or sulfur, to yield the compound of formula IIo or IIo_1, respectively,


(IIo) or

(IIo_1),

wherein R_1, R_2, R_3, R_4, R_{26}, R_{50}, R_{84}, X_4 and X_{19} are as defined, and then, under acid conditions, for example in the presence of acetic acid or propionic acid, and optionally at an elevated temperature of up to 130°C, converting that compound into the compound of formula IW_{6b} or IW_{16b}


(IW_{6b}) or

(IW_{16b})

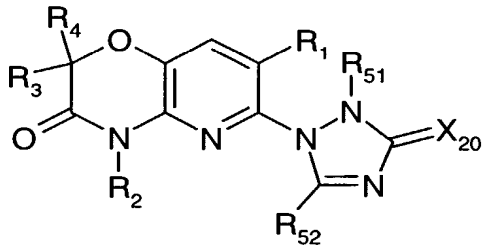
and, using standard processes, carrying out either alkylation (R_2, R_{25} and R_{26} or R_2, R_{49} and R_{50} = alkyl) according to ab) or ac) and/or thionation (X_4, X_{18} and/or X_{19} = S) and optionally alkylation (R_{25}) according to aa) and/or optionally halogenation (R_1, R_{25} = halogen) according to ae), to yield the compounds of formulae IW_6 and IW_{16}


(IW_6) and

(IW_{16}),

wherein R_3, R_4, X_4, X_{18} and X_{19} are as defined, R_1 is hydrogen or halogen, R_{25} is halogen, C_1-C_4alkoxy or C_1-C_4alkylthio and R_2, R_{26}, R_{49} and R_{50} are each independently of the others hydrogen or alkyl. For example, the compound of formula IW_6 wherein R_{26} is other than hydrogen and X_4 is sulfur can be alkylated with the reagent of formula IV

$$R_2\text{-}L_2 \qquad (IV),$$

wherein R_2 is as defined for formula I with the exception of R_2 as hydrogen, and L_2 is a leaving group, for example halogen, especially chlorine, bromine or iodine, in the presence of an alkali metal carbonate. When R_{50} in the compound of formula IW_{16} is hydrogen, that compound can, according to standard processes, be subsequently alkylated (R_{52} = C_1-C_3alkoxy, C_1-C_3alkylthio), thionated (X_{20} = sulfur) and/or halogenated (R_1, R_{52} = halogen) to yield the compound of formula IW_{17}

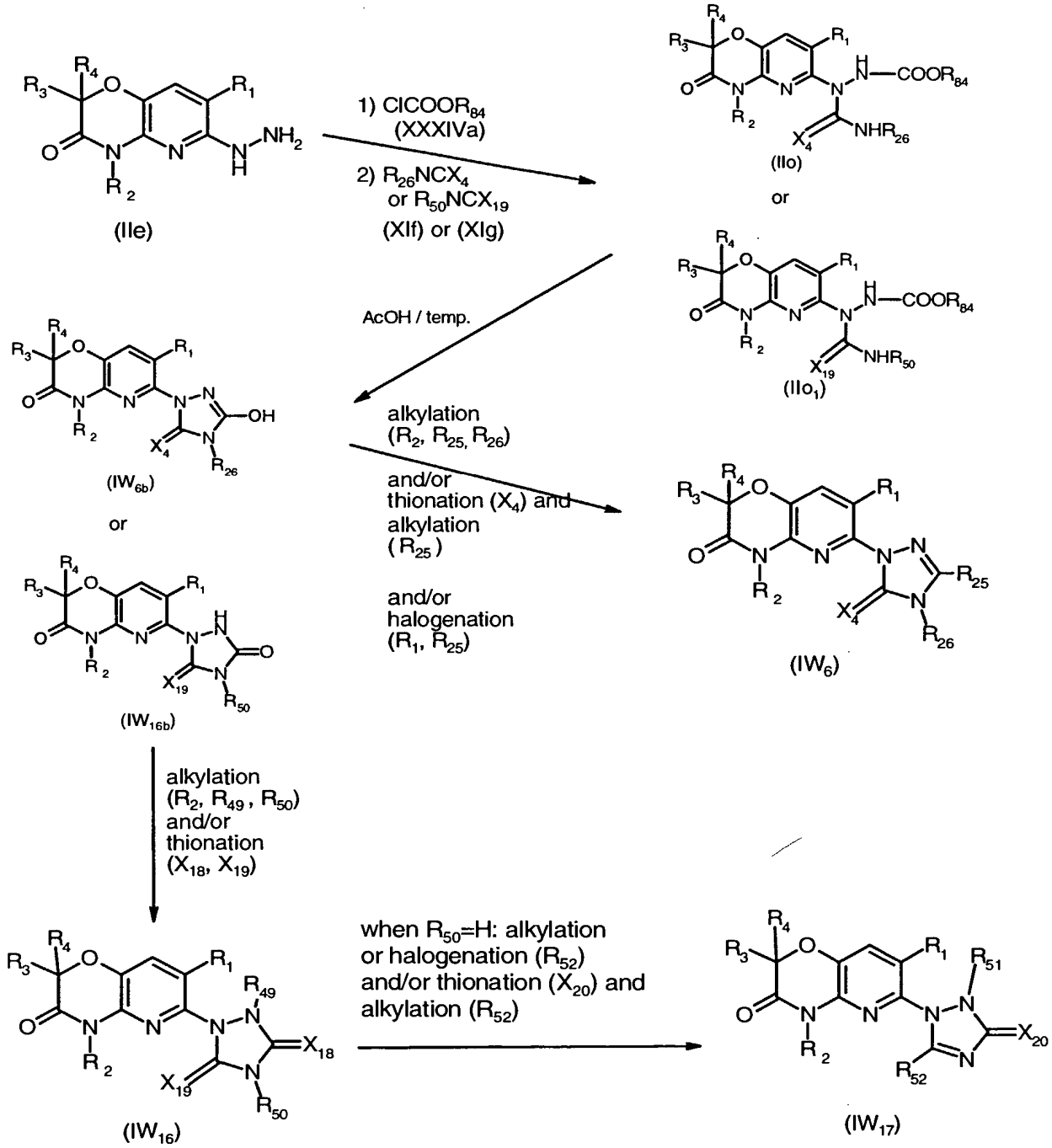


(IW_{17}),

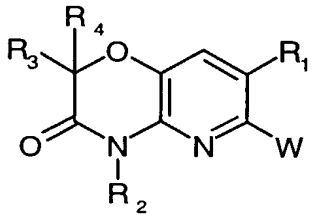
wherein R_1, R_2, R_3 and R_4 are as defined, X_{20} is oxygen or sulfur, R_{51} is C_1-C_4alkyl and R_{52} is halogen, C_1-C_3alkoxy or C_1-C_3alkylthio. Reaction Scheme 6a illustrates those reactions.

The above reaction sequence is especially suitable for preparing compounds of formula IW_6 wherein R_{25} is hydroxy, halogen, C_1-C_4alkoxy, C_1-C_4haloalkoxy, C_1-C_4alkylthio, C_1-C_4haloalkylthio, C_1-C_4alkylsulfinyl, C_1-C_4haloalkylsulfinyl, C_1-C_4alkylsulfonyl, C_1-C_4haloalkylsulfonyl or cyano and also for compounds of formulae IW_{16} and IW_{17} wherein R_{49}, R_{50}, R_{51}, R_{52}, X_{18}, X_{19} and X_{20} are as defined above.

Reaction Scheme 6a:

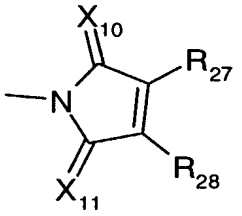


The process according to the invention for the preparation of compounds of formula I is carried out analogously to known processes, as described, for example, in DE-OS-3 917 469 and WO 00/15633, and comprises, for the preparation of those compounds of formula I



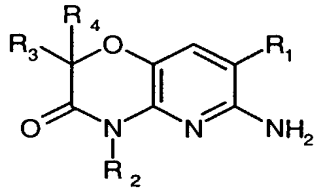
(I)

wherein R_1, R_2, R_3 and R_4 are as defined for formula I and W is a group W_7



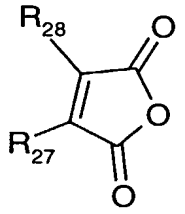
(W_7),

wherein R_{27}, R_{28}, X_{10} and X_{11} are as defined for formula I, reacting a compound of formula IIa



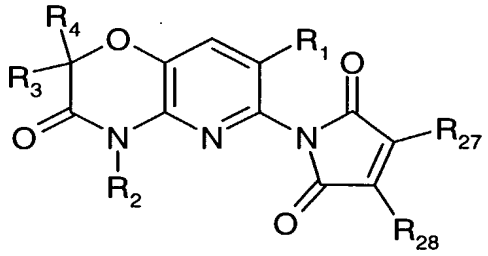
(IIa) ,

wherein R_1, R_2, R_3 and R_4 are as defined for formula I, in the presence of a C_1-C_4alkylcarboxylic acid, for example acetic acid or propionic acid, optionally in an inert solvent, for example a halogenated hydrocarbon, e.g. chlorobenzene, with a compound of formula XXXIII



(XXXIII),

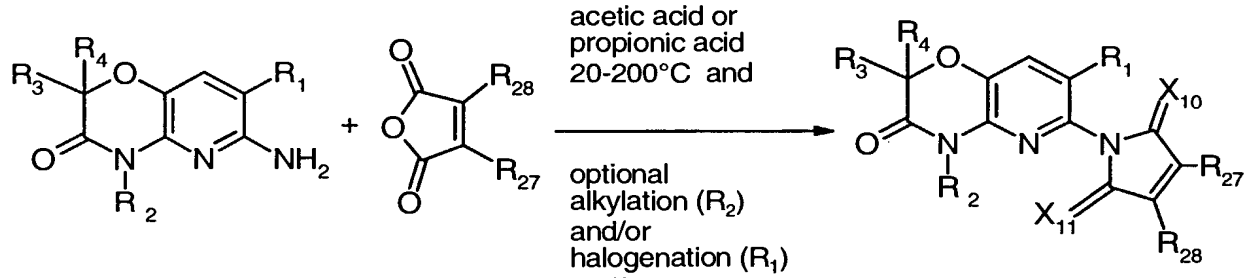
wherein R_{27} and R_{28} are as defined for formula I, in a temperature range of from 20° to 200°C. Reaction Scheme 7 and Example P15 illustrate that reaction sequence. The resulting compound of formula IW_{7a}



(IW$_{7a}$),

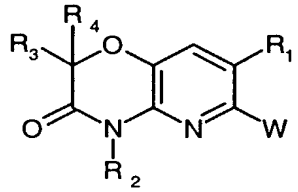
wherein, for example, R_1 and/or R_2 are hydrogen, may be further functionalised according to the definitions of R_1, R_2, X_{10} and X_{11} in accordance with processes described under aa), ac) and ae) to form compounds of formula IW$_7$.

Reaction Scheme 7:



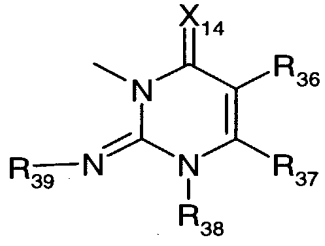
(IIa) (XXXIII) (IW$_{7a}$): e.g. R_1, R_2=H, X_{10}, X_{11}=O (IW$_7$)

The process according to the invention for the preparation of compounds of formula I is carried out analogously to known processes, as described, for example, in WO 00/15633, and comprises, for the preparation of those compounds of formula I



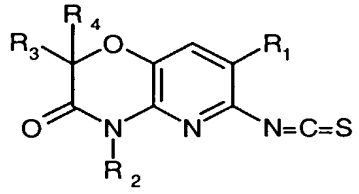
(I)

wherein R_1, R_2, R_3 and R_4 are as defined for formula I and W is a group W_{11}



(W_{11}),

wherein R_{36}, R_{37}, R_{38} and R_{39} are as defined for formula I and X_{14} is oxygen (compound of formula IW_{11a} in Reaction Scheme 17), either, according to route o) in Reaction Scheme 17, reacting a compound of formula IId_4

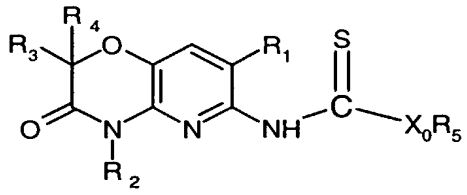


(IId_4),

wherein R_1, R_2, R_3 and R_4 are as defined, with a compound of formula XXXVIII

R_5X_0H (XXXVIII),

wherein R_5 is C_1-C_4alkyl and X_0 is oxygen, sulfur or amino, to yield the compound of formula IIc_4



(IIc_4)

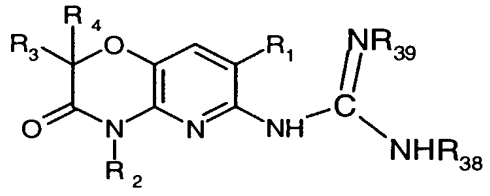
and further reacting that compound in succession with the amines of formulae XXXVIIIa and XXXVIIIb

$R_{38}NH_2$ (XXXVIIIa) and $R_{39}NH_2$ (XXXVIIIb),

or with the diamine derivative of formula XXXVIIIc

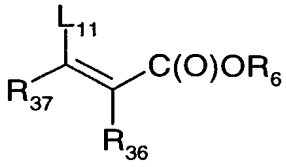
H_2N-R_{38}-R_{39}-NH_2 (XXXVIIIc),

wherein in the compounds of formulae XXXVIIIa and XXXVIIIb R_{38} is C_1-C_3alkyl and R_{39} is hydrogen or C_1-C_3alkyl and in the compound of formula XXXVIIIc R_{38} and R_{39} together form a C_2- or C_3-alkylene bridge, to form the open-chain or cyclic amine derivative of formula IIq



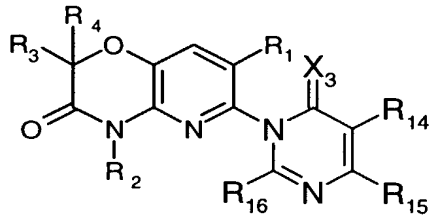
(IIq),

wherein R_1, R_2, R_3, R_4, R_{38} and R_{39} are as defined, and then condensing that compound with a compound of formula XXV



(XXV),

wherein R_{36} and R_{37} are as defined, R_6 is C_1-C_4alkyl and L_{11} is hydroxy, C_1-C_3alkoxy, chlorine, amino or C_1-C_3alkylamino, or, according to route p) in Reaction Scheme 17, first of all reacting a compound of formula IW_2

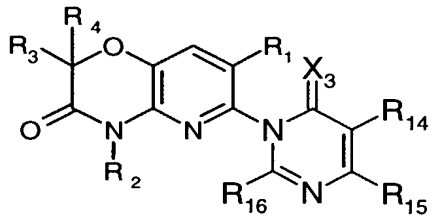


(IW_2),

wherein R_1, R_2, R_3, R_4, X_3, R_{14} and R_{15} are as defined for formula I and R_{16} is C_1-C_3alkylthio, with an oxidising agent, for example hydrogen peroxide, to form the corresponding C_1-C_3alkylsulfonyl derivative of formula IW_2 wherein R_{16} is C_1-C_3alkylsulfonyl, and converting that derivative, by means of aminolysis, for example using gaseous ammonia in ethanol, or using aqueous ammonium hydroxide, or using an amine of formula XXXVIIId or XXXVIIId$_1$

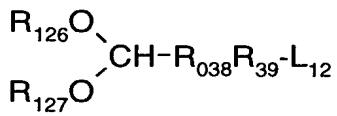
$R_{016}NH_2$ (XXXVIIId) or $(R_{016})_2NH$ (XXXVIIId$_1$),

wherein R_{016} is hydrogen, C_1-C_3alkyl, allyl or propargyl, into the compound of formula IW_2



(IW_2),

wherein R_1, R_2, R_3, R_4, X_3, R_{14} and R_{15} are as defined and R_{16} is amino, C_1-C_3alkylamino, di(C_1-C_3alkyl)amino, allylamino, diallylamino, propargylamino or dipropargylamino, and then reacting that compound, when R_{16} is amino, with an aldehyde derivative of formula XXVIa



(XXVIa),

wherein R_{126} is C_1- or C_2-alkyl and R_{127} is hydrogen or C_1- or C_2-alkyl, R_{038} and R_{39} together form a C_1- or C_2-alkylene bridge and L_{12} is a leaving group, for example chlorine, bromine, iodine, mesyloxy or tosyloxy, or with the reagent of formula XXVIb

L_{13}-$R_{38}R_{39}$-L_{12} (XXVIb),

wherein R_{38} and R_{39} together form a C_2- or C_3-alkylene bridge, L_{12} and L_{13} are each a leaving group, for example chlorine, bromine, iodine, mesyloxy or tosyloxy, or with the alkylating agent of formula XXVId

R_{38}-L_{12} (XXVId),

wherein R_{38} is C_1-C_3alkyl and L_{12} is a leaving group, for example chlorine, bromine or iodine, or a sulfonate, especially mesyloxy or tosyloxy, or, according to route q) in Reaction Scheme 17, first of all reacting the compound of formula IW_2 with an oxidising agent, for example hydrogen peroxide, and then with a reagent of formula XXVIc

H_2N-$R_{39}R_{38}$-L_{13} (XXVIc),

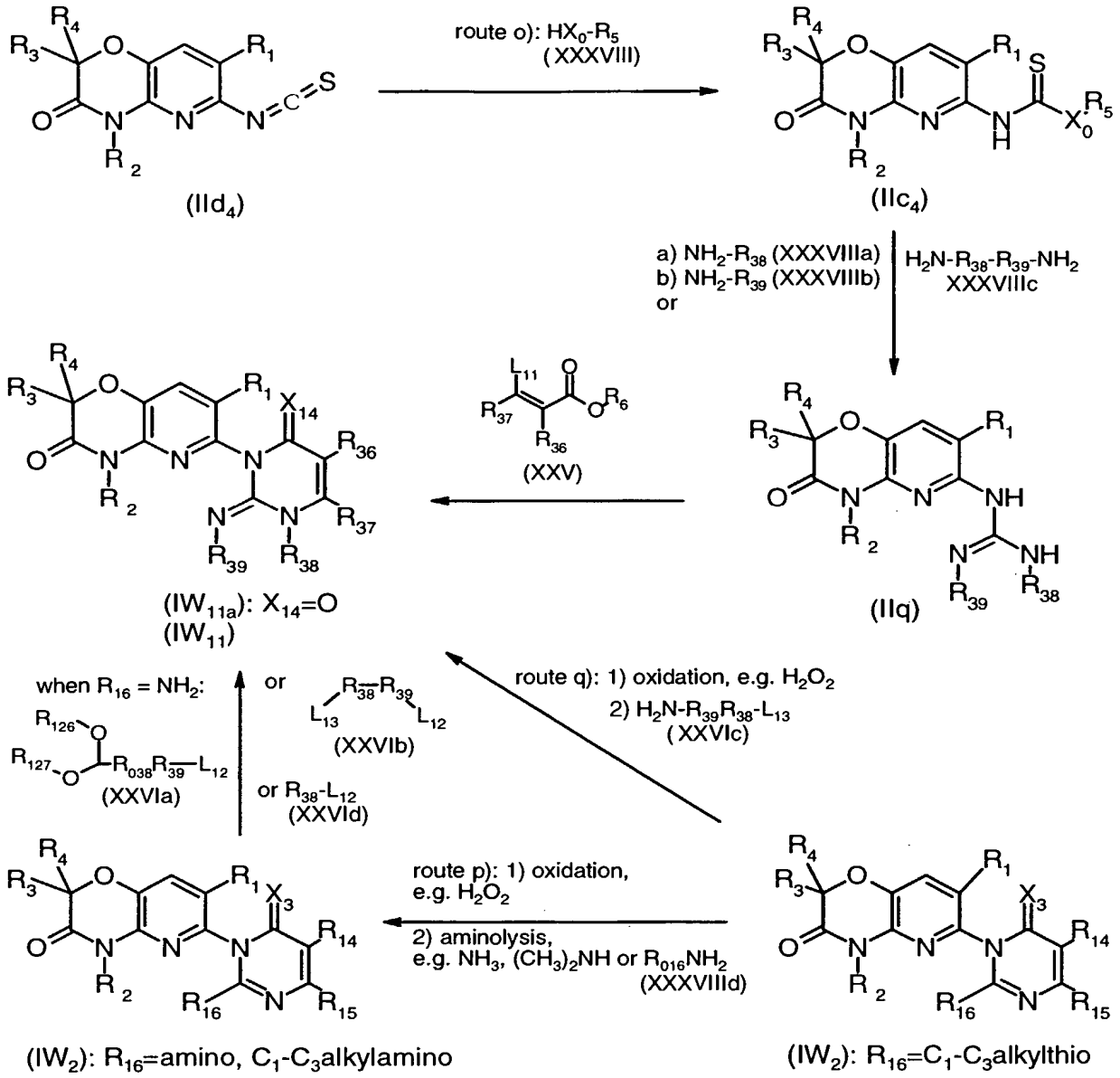
wherein R_{38} and R_{39} together form a C_2- or C_3-alkylene bridge and L_{13} is as defined, wherein according to routes p) and q) in Reaction Scheme 17 the substituents X_{14}, R_{36} and R_{37} in compounds of formulae IW_{11} and IW_{11a} take the meanings of the corresponding substituents X_3, R_{14} and R_{15}, respectively, in the starting compound IW_2, and R_{38} and R_{39} together form a C_2- or C_3-alkylene or -alkenylene bridge.

The resulting compounds of formulae IW_{11} and IW_2 wherein R_1, R_2, R_3, R_4, R_{14}, R_{15}, R_{36}, R_{37}, R_{38}, R_{39}, X_3 and X_{14} are as defined and R_{16} is C_1-C_3alkylsulfinyl, C_1-C_3alkylsulfonyl, amino, C_1-C_3alkylamino, di(C_1-C_3alkyl)amino, allylamino or propargylamino, may be further functionalised in accordance with the standard methods described above: when X_{14} or X_3 is oxygen, in accordance with aa) using a thionating reagent; when R_{38} is hydrogen, in accordance with ab) using an alkylating reagent of formula IXa

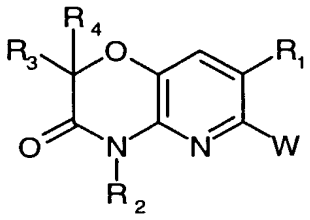
R_{38}-L_1 (IXa),

wherein R_{38} is as defined for formula I and L_1 is a leaving group, for example halogen, especially chlorine, bromine or iodine, or a sulfonate, especially mesyloxy or tosyloxy; when R_2 is hydrogen, in accordance with ac) using an alkylating reagent of formula IV; and, when R_1 and/or R_{36} are hydrogen, in accordance with ae) using a halogenating reagent.

Reaction Scheme 17:

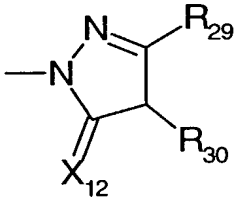


The process according to the invention for the preparation of compounds of formula I is carried out analogously to known processes, as described, for example, in DE-OS-3 917 469, WO 00/15633 and US-A-4 831 150, and comprises, for the preparation of those compounds of formula I

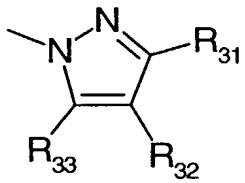


(I)

wherein R_1, R_2, R_3 and R_4 are as defined for formula I and W is a group W_8 or W_9

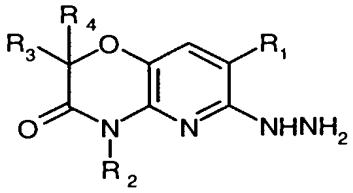


(W_8) or



(W_9),

wherein R_{29}, R_{30}, R_{31}, R_{32}, R_{33} and X_{12} are as defined for formula I, condensing with one another a compound of formula IIe

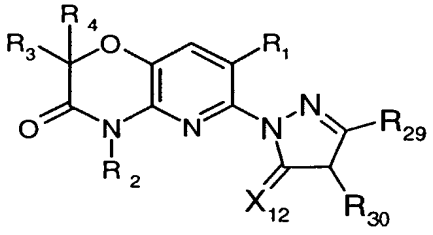


(IIe),

wherein R_1, R_2, R_3 and R_4 are as defined, and a compound of formula XIh

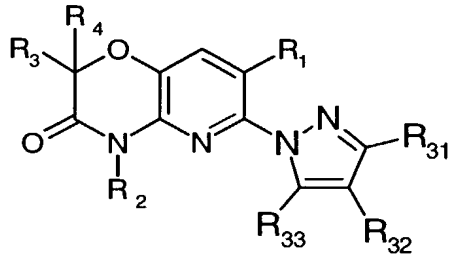
$$R_{85}OC(X_{12})\text{-}CH(R_{30})\text{-}COR_{29} \qquad \text{(XIh)},$$

wherein R_{29}, R_{30} and X_{12} are as defined and R_{85} is C_1-C_4alkyl or phenyl, optionally in an organic acid, for example acetic acid or propionic acid, and a further inert solvent, for example a halogenated hydrocarbon, e.g. chlorobenzene, by heating at from 20° to 200°C to yield the compound of formula IW_8



(IW_8)

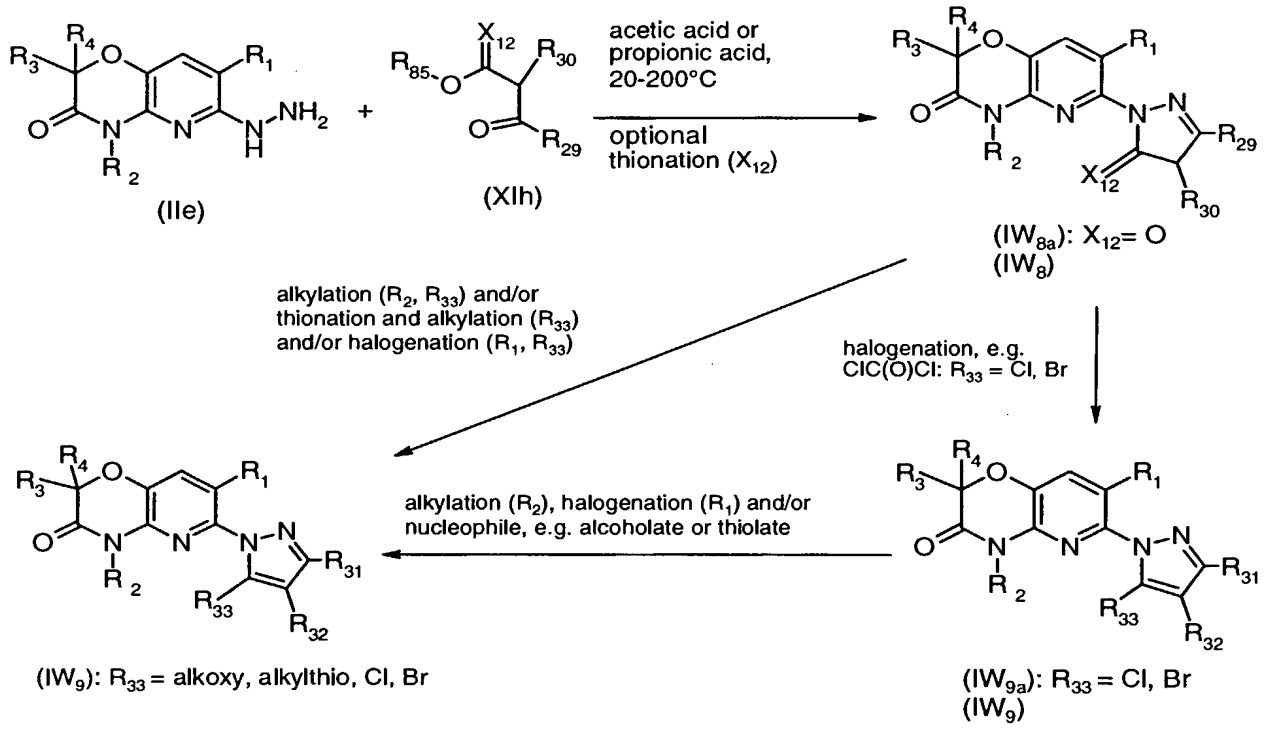
That compound may be further functionalised in accordance with the standard methods aa), ac) and/or ae) described above. In particular, it is possible, starting from the compound of formula IW_8, to obtain, by means of halogenation, for example using phosgene, oxalyl chloride, thionyl chloride, phosphorus oxychloride or phosphorus pentachloride, phosphorus oxybromide or phosphorus tribromide (R_1, R_{33}), and/or alkylation (R_2, R_{33}) and/or thionation and alkylation (R_{33}), the compound of formula IW_9



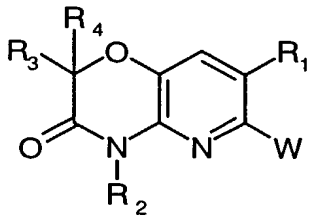
(IW_9)

wherein R_1, R_2, R_3 and R_4 are as defined, R_{31} and R_{32} have the meanings of R_{29} and R_{30}, respectively, in the compound of formula IW_8 and R_{33} is halogen, hydroxy, C_1-C_3alkoxy, C_1-C_3haloalkoxy, mercapto, C_1-C_3alkylthio, C_1-C_3alkylsulfinyl or C_1-C_3alkylsulfonyl. Reaction Scheme 10 illustrates those reaction steps.

Reaction Scheme 10:

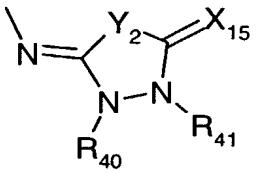


The process according to the invention for the preparation of compounds of formula I is carried out analogously to known processes and comprises, for the preparation of those compounds of formula I



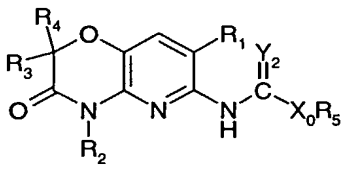
(I)

wherein R_1, R_2, R_3 and R_4 are as defined for formula I and W is a group W_{12}

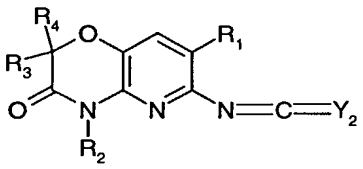


(W_{12}),

wherein R_{40}, R_{41}, X_{15} and Y_2 are as defined for formula I, reacting a compound of formula IId_3 or IIc_3



(IIc_3) or

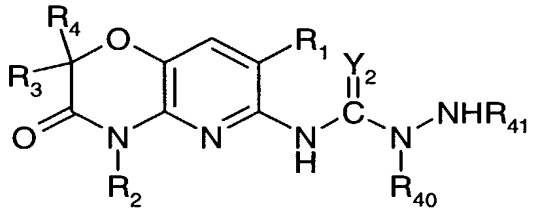


(IId_3),

wherein R_1, R_2, R_3, R_4 and Y_2 are as defined for formula I, R_5 is C_1-C_4alkyl and X_0 is oxygen, sulfur or amino, with a compound of formula XXXV

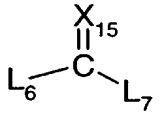
R_{40}-NH-NH-R_{41} (XXXV),

wherein R_{40} and R_{41} are as defined for formula I, to yield the compound of formula IIp_1



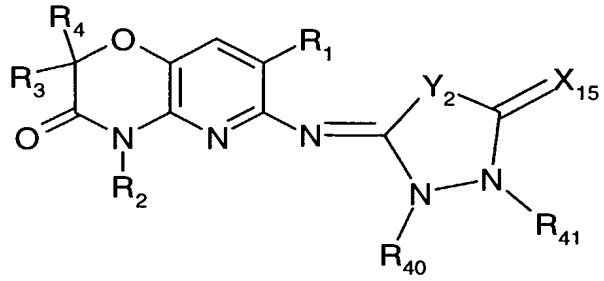
(IIp_1),

and further reacting that compound with the compound of formula XXXVI



(XXXVI),

wherein X_{15} is oxygen or sulfur, and L_6 and L_7 are leaving groups, for example halogen, e.g. chlorine or bromine (phosgene, thiophosgene), or L_7 may additionally be hydroxy or C_1-C_4alkoxy (haloformic acid or an ester thereof). That (thio)phosgenation reaction is carried out at temperatures of from 0° to 80°C, preferably from 5° to 25°C. Reaction Scheme 8 illustrates that reaction sequence. The resulting compounds of formula IW_{12}



(IW$_{12}$),

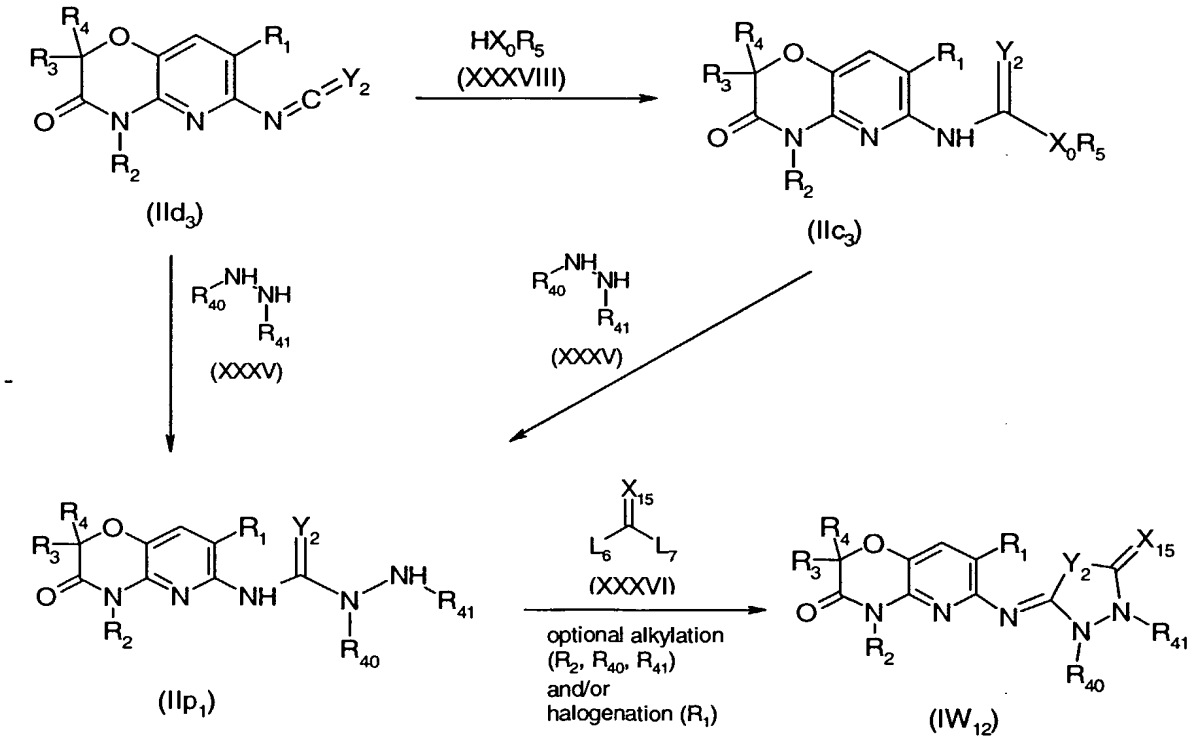
wherein, for example, R_1, R_2, R_{40} and R_{41} are hydrogen and X_{15} is oxygen, may be further functionalised according to the definitions of R_1, R_2, R_{40}, R_{41} and X_{15} in accordance with processes described under aa), ac), ad) and ae).

The iso(-thio-)cyanate derivative of formula IId$_3$ may, in addition, be converted into the compound of formula IIc$_3$ by reaction with a reagent of formula XXXVIII

R_5X_0H (XXXVIII),

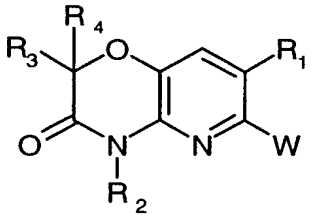
wherein R_5 is C_1-C_4alkyl and X_0 is oxygen, sulfur or amino.

Reaction Scheme 8:



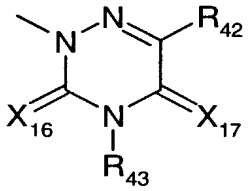
The process according to the invention for the preparation of compounds of formula I is carried out analogously to known processes, as described, for example, in Helv. Chim. Acta

61, 1175 (1978), J. Heterocycl. Chem. 17, 1365 (1980) and WO 97/30980, and comprises, for the preparation of those compounds of formula I



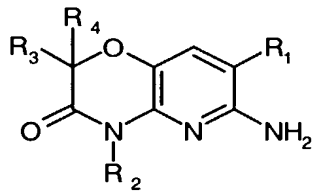
(I)

wherein R_1, R_2, R_3 and R_4 are as defined for formula I and W is a group W_{13}



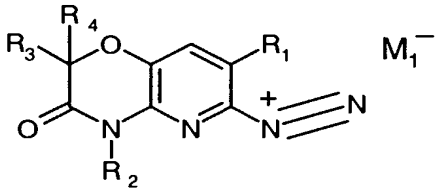
(W_{13}),

wherein R_{42}, R_{43}, X_{16} and X_{17} are as defined for formula I, first of all converting a compound of formula IIa



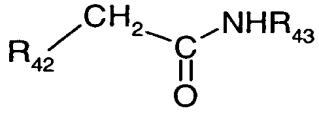
(IIa) ,

wherein R_1, R_2, R_3 and R_4 are as defined for formula I, under diazotisation conditions, into the diazonium salt of formula IIee



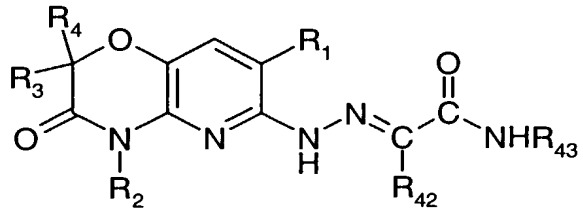
(IIee),

wherein R_1, R_2, R_3 and R_4 are as defined and M_1^- is an anion, for example hydrogen sulfate or tetrafluoroborate, or halide, for example chloride, and then, in accordance with route m) in Reaction Scheme 9, coupling that salt with the reagent of formula XXXVIIa



(XXXVIIa),

wherein R_{42} and R_{43} are as defined, to form the hydrazone derivative of formula IIk

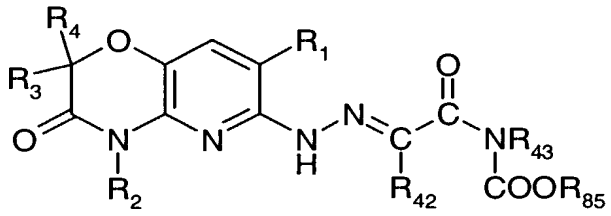


(IIk)

and further reacting that derivative with the chloroformic acid ester of formula XXXIVb

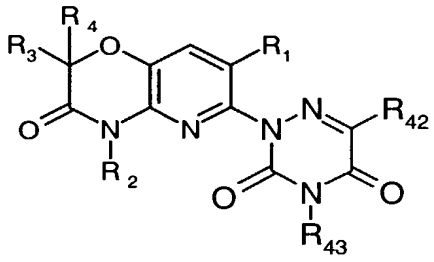
$ClCOOR_{85}$ (XXXIVb),

wherein R_{85} is C_1-C_4alkyl, to form the compound of formula III



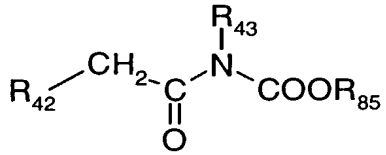
(III),

which is cyclised under basic conditions, for example in aqueous sodium or potassium hydroxide solution, to form the compound of formula IW_{13a}



(IW_{13a}),

or, in accordance with route n) in Reaction Scheme 9, the diazonium salt of formula IIee may be coupled with the reagent of formula XXXVIIb



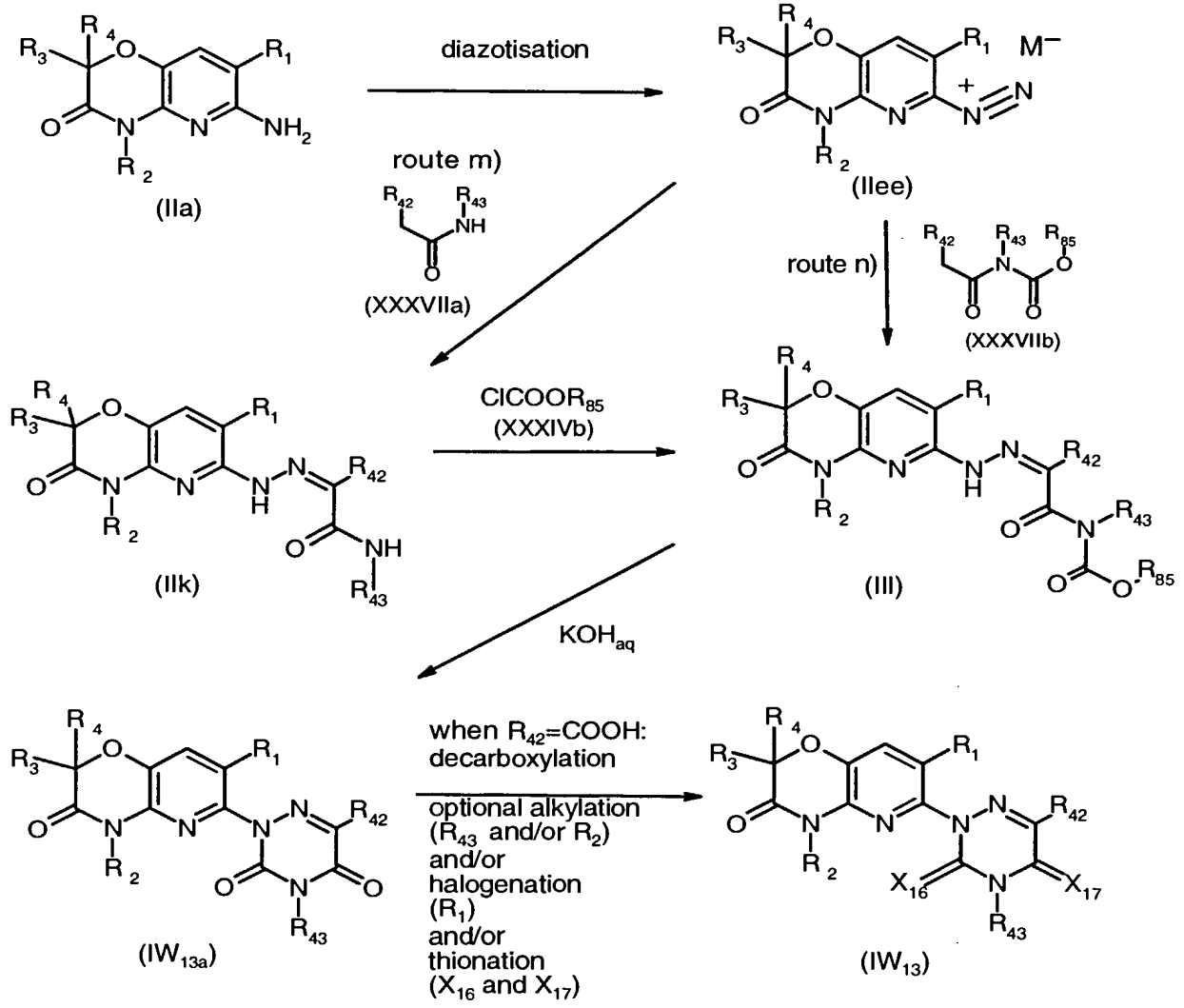
(XXXVIIb),

wherein R_{42}, R_{43} and R_{85} are as defined, to form the compound of formula III directly, which may then be cyclised analogously to route m), under basic conditions, to form the compound of formula IW_{13a}.

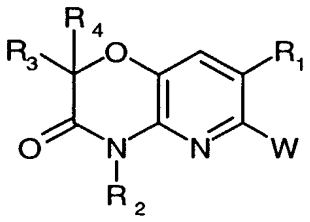
The resulting compounds of formula IW_{13a} wherein, for example, R_{42} is a carboxyl group may be converted into the compounds of formula IW_{13} wherein R_{42} is hydrogen using standard decarboxylation methods, for example by heating in an aqueous mineral acid, e.g.

hydrochloric acid, or in the presence of a carboxylic acid, e.g. oxalic acid or thioglycolic acid, in an organic solvent, for example a halogenated hydrocarbon, e.g. chlorobenzene. Furthermore, the compounds of formula IW_{13a} wherein R_{43} and/or R_2 are hydrogen or R_1 is hydrogen may be further functionalised according to the definitions of R_1, R_2, R_{43}, X_{16} and X_{17} by means of alkylation and/or halogenation, as described under ab) and ac) in the former case and ae) in the latter case, or, when X_{16} and X_{17} in the compound of formula IW_{13} are sulfur, by means of thionation as described under aa). Reaction Scheme 9 illustrates those reaction sequences.

Reaction Scheme 9:

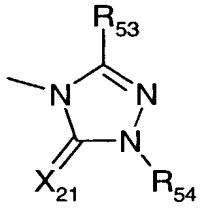


The process according to the invention for the preparation of compounds of formula I is carried out analogously to known processes, as described, for example, in EP-A-0 726 258, and comprises, for the preparation of those compounds of formula I



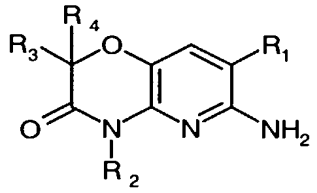
(I)

wherein R_1, R_2, R_3 and R_4 are as defined for formula I and W is a group W_{18}



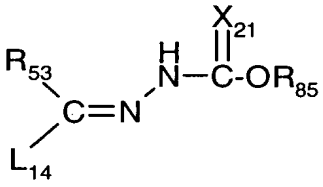
(W_{18}),

wherein R_{53}, R_{54}, and X_{21} are as defined for formula I, reacting a compound of formula IIa



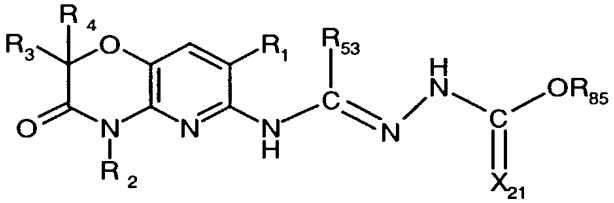
(IIa) ,

wherein R_1, R_2, R_3 and R_4 are as defined, with a hydrazinecarboxylic acid ester of formula XIVa



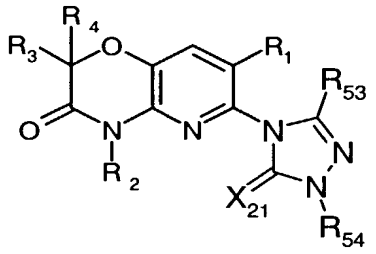
(XIVa),

wherein R_{53} and X_{21} are as defined, R_{85} is C_1-C_4alkyl and L_{14} is a leaving group, for example halogen, e.g. chlorine or bromine, to form the compound of formula IIr



(IIr)

and heating that compound in the presence of an alkali metal hydroxide solution and cyclising that compound to form the compound of formula IW_{18}



(IW$_{18}$),

wherein R_1, R_2, R_3, R_4, R_{53} and X_{21} are as defined and R_{54} is hydrogen, and carrying out a further reaction with the alkylating reagent of formula XVII

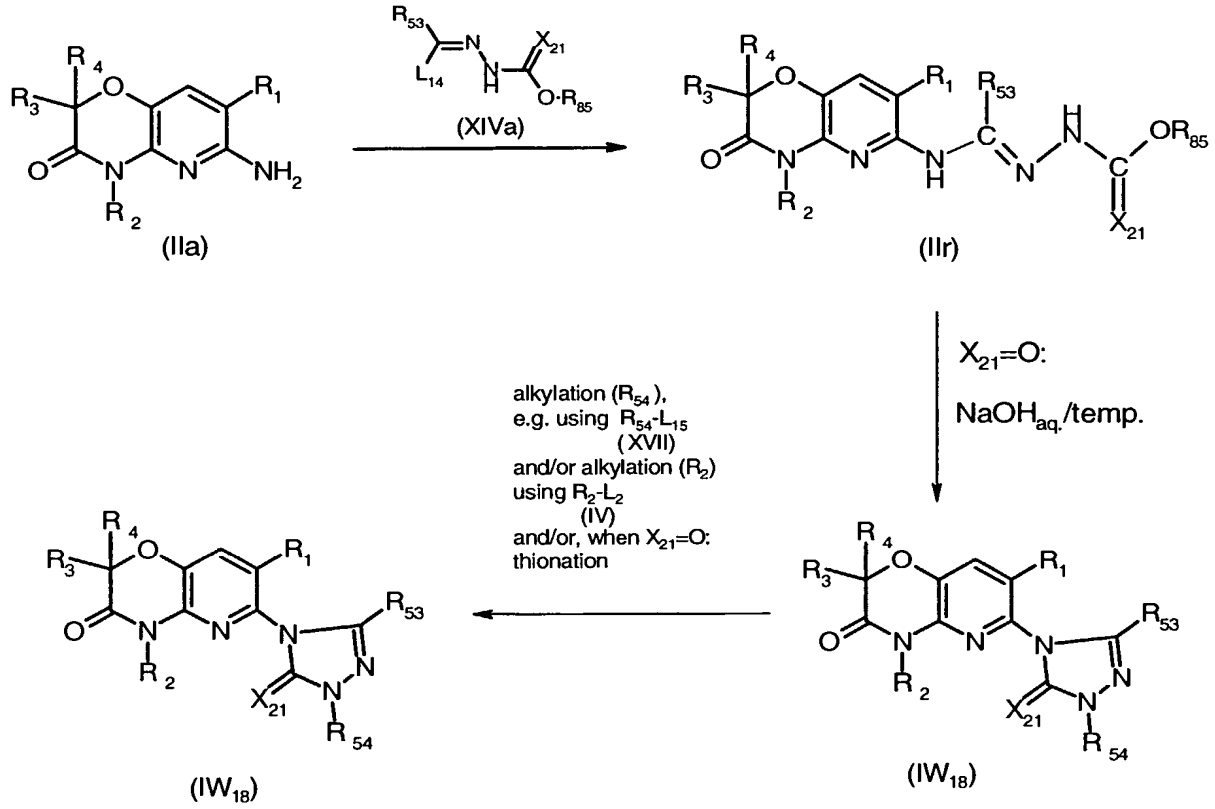
$$R_{54}\text{-}L_{15} \qquad \text{(XVII)},$$

wherein R_{54} is C_1-C_3alkyl and L_{15} is a leaving group, for example halogen, especially chlorine, bromine or iodine, or a sulfonate, especially mesyloxy or tosyloxy, and/or, when R_2 is hydrogen, optionally carrying out a reaction, as described under ac) above, with the alkylating reagent of formula IV

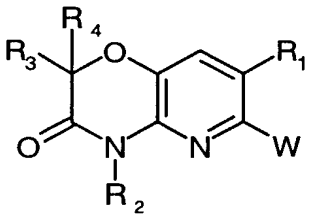
$$R_2\text{-}L_2 \qquad \text{(IV)},$$

wherein R_2 is as defined for formula I with the exception of R_2 as hydrogen and L_2 is a leaving group, and/or, when X_{21} is oxygen, carrying out thionation as described under aa) above. Reaction Scheme 18 illustrates those reactions.

Reaction Scheme 18:

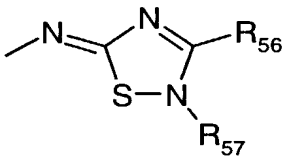


The process according to the invention for the preparation of compounds of formula I is carried out analogously to known processes, as described, for example, in J. Pestic. Sci. 18, 309 (1993), and comprises, for the preparation of those compounds of formula I



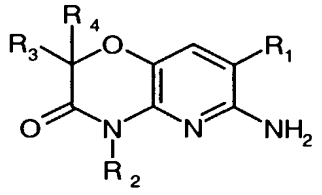
(I)

wherein R_1, R_2, R_3 and R_4 are as defined for formula I and W is a group W_{20}



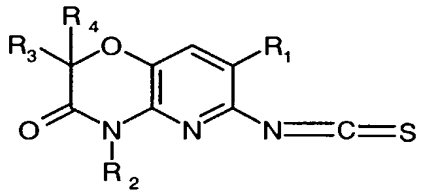
(W_{20}),

wherein R_{56} and R_{57} are as defined for formula I, first of all converting a compound of formula IIa



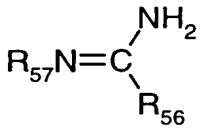
(IIa) ,

wherein R_1, R_2, R_3 and R_4 are as defined, for example using thiophosgene, into the isothiocyanate of formula IId_4



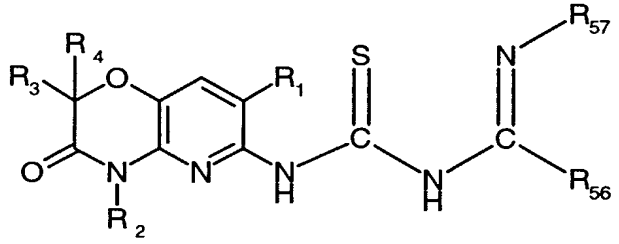
(IId_4)

and then further reacting that isothiocyanate with an amidine derivative of formula XVIII



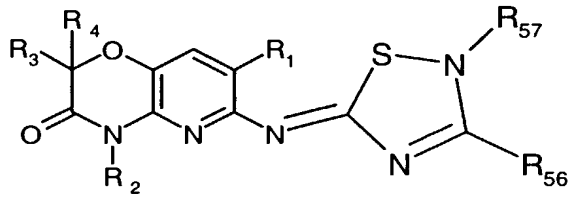
(XVIII),

wherein R_{56} and R_{57} are as defined, to yield the compound of formula IIs



(IIs),

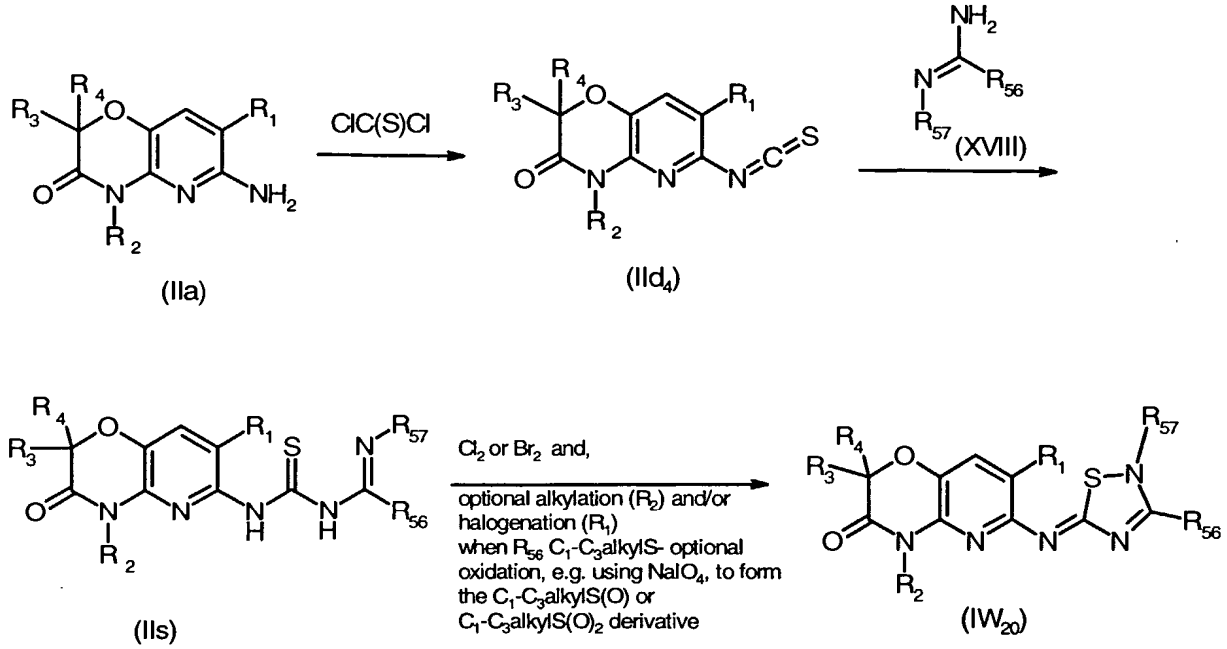
which, on treatment with chlorine or bromine, is cyclised to form the compound of formula IW_{20}



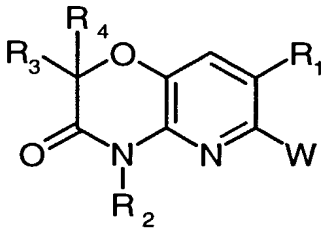
(IW_{20})

and is optionally alkylated (R_2) and/or halogenated (R_1) in accordance with standard processes as described under ac) and ae) and, when R_{56} is C_1-C_3alkylthio, is optionally oxidised using an oxidising agent, for example sodium periodate, to form the corresponding C_1-C_3alkylsulfinyl or C_1-C_3alkylsulfonyl derivative. Reaction Scheme 19 illustrates those reactions.

Reaction Scheme 19:

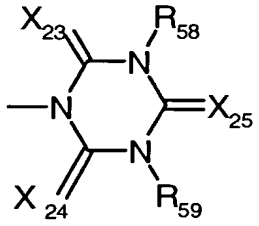


The process according to the invention for the preparation of compounds of formula I is carried out analogously to known processes, as described for example in DE 3516631 or DE 2718799, or in C. R. Hebd. Seances Acad. Sci., Ser. C (1976), 283, 491, for the preparation of those compounds of formula I



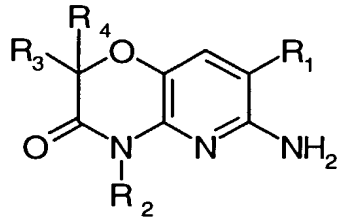
(I) ,

wherein R_1, R_2, R_3 and R_4 are as defined for formula I, and W is a group W_{21}



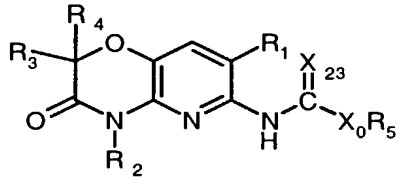
(W_{21}),

wherein R_{58}, R_{59}, X_{23}, X_{24} and X_{25} are as defined for formula I, first of all converting a compound of formula IIa

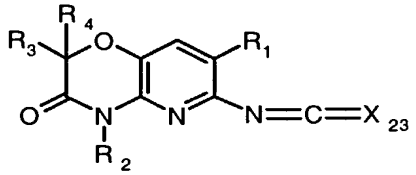


(IIa) ,

wherein R_1, R_2, R_3 and R_4 are as defined for formula I, either, according to Reaction Scheme 21, by reacting a compound of formula IIc_7 or IId_7

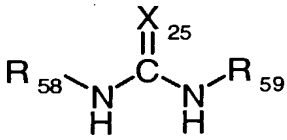


(IIc_7) or



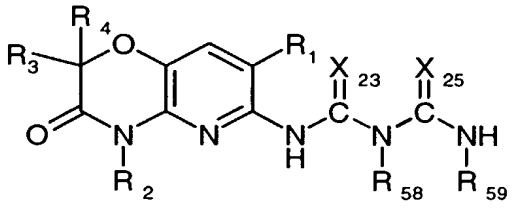
(IId_7),

wherein R_1, R_2, R_3, R_4 and X_{23} are as defined for formula I, X_0 is oxygen, and R_5 is C_1-C_4alkyl, with an urea of formula XXXVb



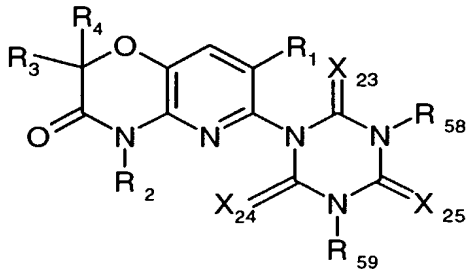
(XXXVb) ,

wherein R_{58}, R_{59} and X_{25} are as defined for formula I, in the presence of a base, for example a trialkylamine, and a suitable solvent, for example a chlorinated hydrocarbon, e.g. chlorobenzene, or an amide, e.g. DMF or NMP, to thereby yield the compound of formula IIt_1



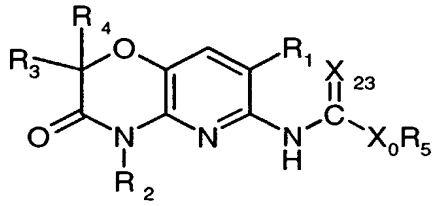
(IIt_1) ,

wherein R_1, R_2, R_3, R_4, R_{58}, R_{59}, X_{23} and X_{25} are as defined, and then cyclising that compound in the presence of a carbonyl equivalent like phosgene, diphosgene, ethylchloroformiate (compound of formula VIc), carbonyldiimidazol (CDI), carbonylbistriazol, to form the compound of formula IW_{21}



(IW$_{21}$),

or according to Reaction Scheme 21, reacting a compound of formula IIc$_7$

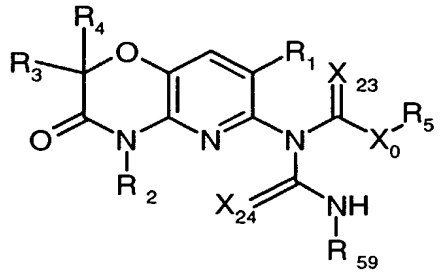


(IIc$_7$) ,

wherein R_1, R_2, R_3, R_4 and X_{23} are as defined for formula I, X_0 is oxygen, and R_5 is C_1-C_4alkyl, firstly in a suitable solvent, for example a chlorinated hydrocarbon, e.g. chlorobenzene, or an amide, e.g. DMF or NMP, with an isocyanate or an isothiocyanate of the formula XIo

$$X_{24}=C=N-R_{59} \qquad \text{(XIo)},$$

wherein R_{59} and X_{24} are as defined for formula I, to thereby yield the compound of formula IIt$_2$

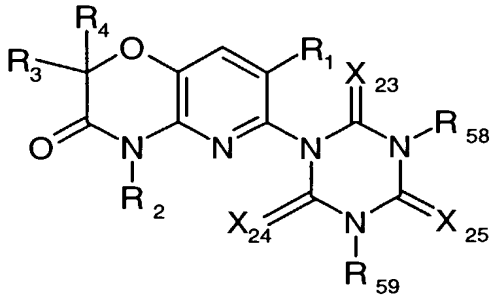


(IIt$_2$),

wherein R_1, R_2, R_3, R_4, R_5, R_{59}, X_{23} and X_{24} are as defined, X_0 is oxygen, and R_5 is C_1-C_4alkyl, and then cyclising that compound in the presence of an isocyanate or an isothiocyanate of formula XIp

$$X_{25}=C=N-R_{58} \qquad \text{(XIp)},$$

wherein R_{58} and X_{25} are as defined for formula I, to form the compound of formula IW$_{21}$



(IW_{21}) .

The compound of formula IW_{21} may, optionally, be further functionalised according to the definitions of R_1, R_2, R_{58}, R_{59}, X_{23}, X_{24} and X_{25} in analogous manner to that described under aa), ac) or ae).

For example, the compound of formula IW_{21}, wherein R_{58} and/or R_{59} are hydrogen, can be further reacted, in analogous manner to that described under ac), with an alkylating reagent of formula XVc and/or XVd

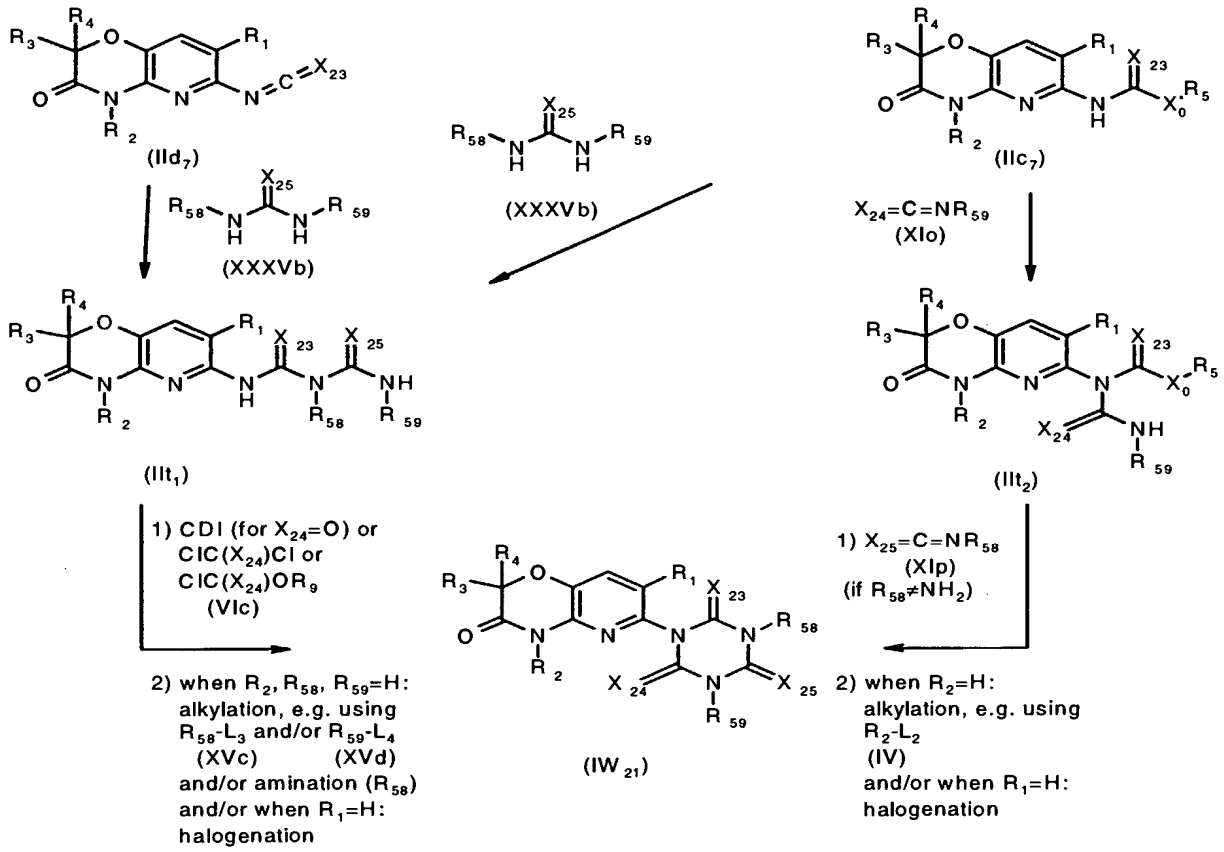
R_{58}-L_3 (XVc) and/or R_{59}-L_4 (XVd),

wherein R_{58} and R_{59} are as defined for formula I with the exception of R_{58} and R_{59} as hydrogen, and L_3 and L_4 are each a leaving group, for example halogen, especially chlorine, bromine or iodine, or a sulfonate, especially mesyloxy or tosyloxy, in the presence of a suitable base to form the compound of formula IW_{21}, wherein R_{58} and/or R_{59} are C_1-C_3alkyl or C_1-C_3haloalkyl. Optionally, the compound of formula IW_{21}, wherein R_2 is hydrogen, and R_{58} and R_{59} are other than hydrogen can be alkylated in the presence of a base, for example an alkali metal carbonate, e.g. potassium carbonate as acid-binding agent, with the reagent of formula IV

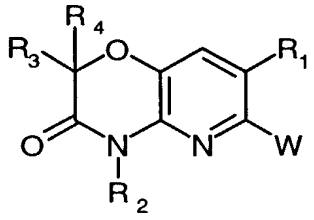
R_2-L_2 (IV),

wherein R_2 is as defined for formula I with the exception of R_2 as hydrogen, and L_2 is a leaving group, for example halogen, e.g. chlorine, bromine or iodine, or sulfonate, e.g. mesyloxy or tosyloxy.

Reaction Scheme 21:

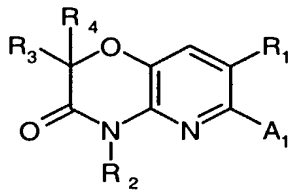


The process according to the invention for the preparation of compounds of formula I according to variant c) and Reaction Scheme 1c) is carried out analogously to known processes and comprises, for the preparation of those compounds of formula I



(I)

wherein R_1, R_2, R_3 and R_4 are as defined for formula I and W is a group W_1 to W_{21} (C-N-linked ring systems), reacting a compound of formula IIb



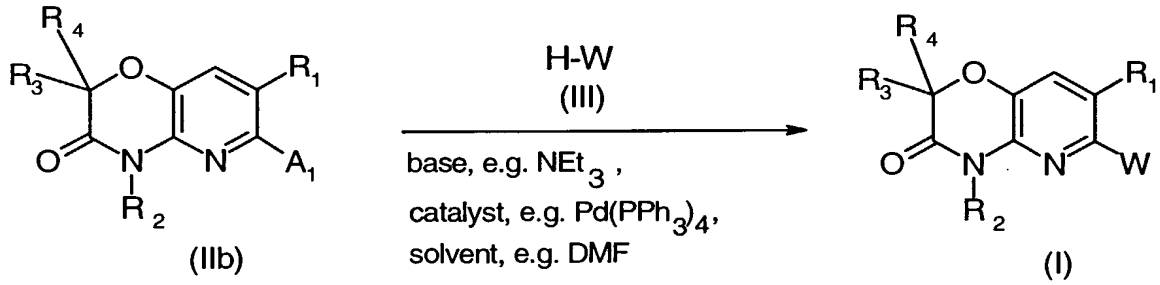
(IIb) ,

wherein R_1, R_2, R_3 and R_4 are as defined and A_1 is a leaving group, for example halogen, especially fluorine, chlorine or bromine, sulfonyl, especially methylsulfonyl, sulfonate, especially trifluoromethylsulfonyloxy, methylsulfonyloxy or phenylsulfonyloxy, or nitro, with an N-heterocyclic compound of formula III

H-W (III),

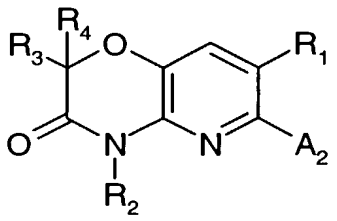
wherein W is a group W_1 to W_{21}, in the presence of a base, for example a trialkylamine, especially triethylamine, a carbonate, especially sodium and potassium carbonate, or also caesium fluoride, in the presence of one or more suitable catalysts, for example metal catalysts, especially palladium catalysts, e.g. tetrakis(triphenylphosphine)palladium ($Pd(PPh_3)_4$), bis(triphenylphosphine)palladium(II) dichloride ($Pd(PPh_3)_2Cl_2$) or palladium(II) acetate ($Pd(OAc)_2$), and/or copper iodide, and further catalytic additives, for example various phosphine ligands, e.g. biphenyl-2-bis-tert-butylphosphine, and in the presence of a suitable diluent, for example an aromatic hydrocarbon, e.g. one of the xylene isomers, or an amide, e.g. NMP or DMF, as illustrated in Reaction Scheme 1c.

Reaction Scheme 1c:



(IIb) (I)

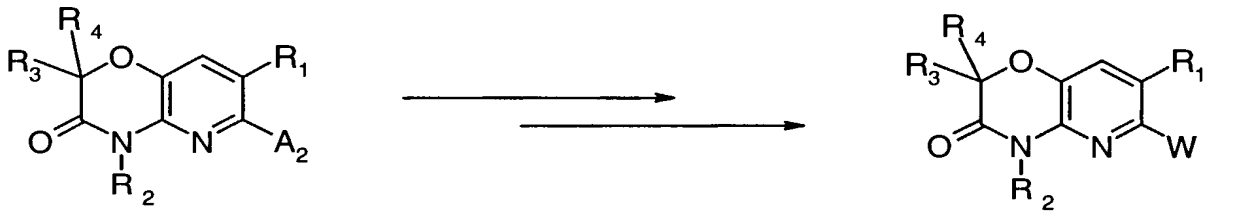
The process according to the invention for the preparation of compounds of formula I wherein W is a group W_{100} to W_{109} (C-C-linked ring systems) is carried out, for example, starting from compounds of formula IIu



(IIu),

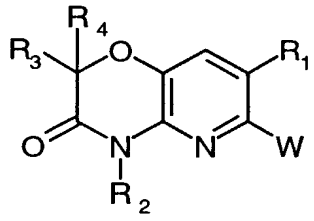
wherein R_1 to R_4 are as defined for formula I and A_2 is methyl, ethyl, ethynyl, cyano, formyl, acyl, carboxy or C_1-C_4alkoxycarbonyl, according to variant d) and Reaction Scheme 1d

Reaction Scheme 1d:



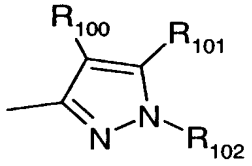
(IIu) (I) ($W=W_{100}$-W_{109})

or analogously to known processes, as described, for example, in EP-A-0 839 808, WO 96/01254 and WO 98/21199, and comprises, for the preparation of those compounds of formula I



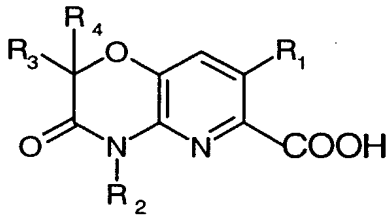
(I)

wherein R_1, R_2, R_3 and R_4 are as defined for formula I and W is a group W_{100}

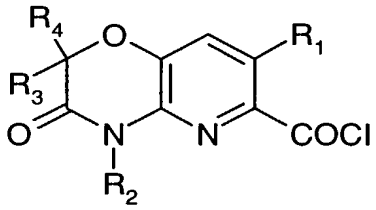


(W_{100}),

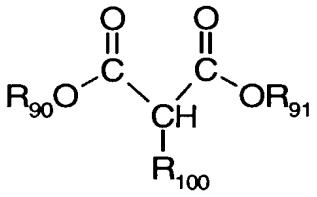
wherein R_{100} is hydrogen, chlorine or bromine, R_{101} is difluoromethoxy and R_{102} is as defined for formula I, converting a compound of formula IIu_1


(IIu$_1$)

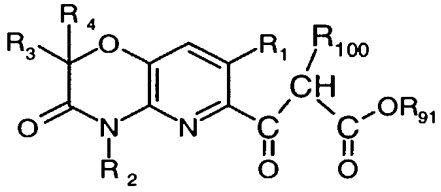
using standard processes, for example using thionyl chloride, oxalyl chloride or phosgene, into the activated form (acid chloride) of formula IIu$_2$


(IIu$_2$) ,

the substituents R_1, R_2, R_3 and R_4 in the compounds of formulae IIu$_1$ and IIu$_2$ being as defined, and reacting the latter compound with a malonic acid ester of formula XL


(XL),

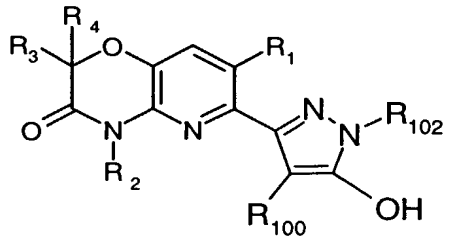
wherein R_{90} is hydrogen, a sodium, potassium or magnesium cation, trimethylsilyl or C_1-C_4alkyl, R_{91} is C_1-C_4alkyl and R_{100} is as defined for formula I, in the presence of a suitable base, for example an alkylamine, e.g. triethylamine, and an inert solvent, for example an amide, e.g. DMF, and subsequent hydrolysis to form the keto ester of formula IIx


(IIx) ,

then cyclising that keto ester with a hydrazine derivative of formula XLI

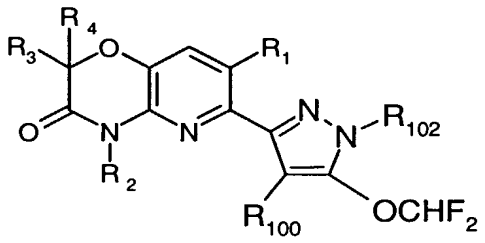
H_2NNHR_{102} (XLI),

wherein R_{102} is as defined for formula I, to form the pyrazolone derivative of formula IW$_{100z}$



(IW_{100z})

and finally subjecting that derivative to a freonisation reaction, for example using chlorodifluoromethane or bromodifluoromethane in the presence of a suitable base, for example an alkali metal hydroxide, especially sodium hydroxide, or a carbonate, especially potassium carbonate, and in a suitable solvent, for example an ether, e.g. tetrahydrofuran or dioxane, or water, or in a two-phase system containing water and a chlorinated hydrocarbon at temperatures of from -10° to 110°C or advantageously in a closed system under slight overpressure and, when R_{100} is hydrogen, optionally to a halogenation reaction, for example using halogen, e.g. chlorine or bromine, or using sulfuryl halide, e.g. sulfuryl chloride, to thereby yield the compound of formula IW_{100a}



(IW_{100a}) ,

R_1, R_2, R_3, R_4 and R_{102} in the compounds of formulae IW_{100z} being IW_{100a} as defined and R_{100} being hydrogen or halogen, and, optionally, further functionalising that compound according to the definitions of R_1, R_2, R_{100} and R_{102} given for formula I in accordance with standard methods.

Compounds of formula IW_{100a} wherein R_2 is hydrogen may, for example, be alkylated, according to process variant ac), using an appropriate alkylating reagent of formula IV

$$R_2\text{-}L_2 \qquad (IV),$$

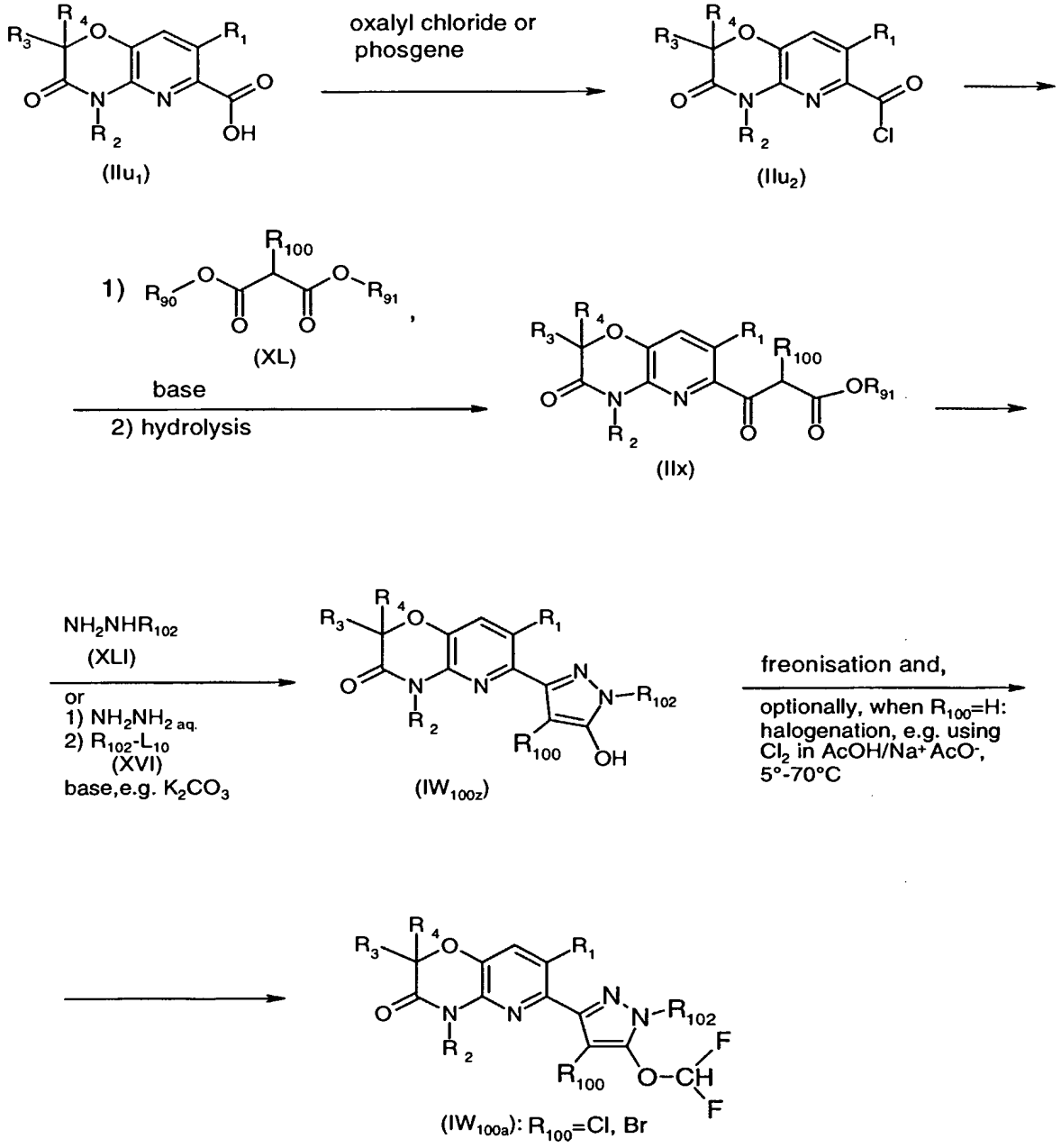
wherein R_2 is as defined for formula I with the exception of R_2 as hydrogen, and L_2 is a leaving group; or compounds of formula IW_{100a} wherein R_1 is hydrogen may, for example, be halogenated according to process variant ae), using a suitable halogenating reagent. The halogenation reaction can advantageously be carried out 'in situ', following on from the freonisation reaction. Chlorination is carried out, for example, by passing an equimolar amount or slight excess of chlorine gas into a suitable solvent system, for example a carboxylic acid, e.g. acetic acid, in the presence of a weak base, for example sodium

acetate, at temperatures of from 5° to 70°C. By that means, compounds of formula IW_{100a} wherein R_{100} is chlorine and R_1 is hydrogen are obtained selectively.

When the above halogenation reaction is carried out using an excess of halogenating reagent, it is possible to obtain, from compounds of formula IW_{100z} wherein R_1 is hydrogen, the corresponding dihalogenated compound of formula IW_{100a} wherein R_1 and R_{100} are halogen, especially chlorine or bromine.

Reaction Scheme 11 illustrates those reactions.

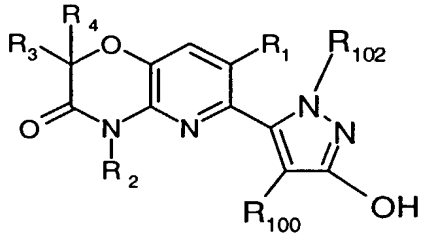
Reaction Scheme 11:



If the keto ester of formula IIx is reacted with hydrazine (compound of formula XLI wherein R_{102} is hydrogen) there is formed the pyrazolone derivative of formula IW_{100z} wherein R_{102} is hydrogen, which, on subsequent alkylation using the reagent of formula XVI

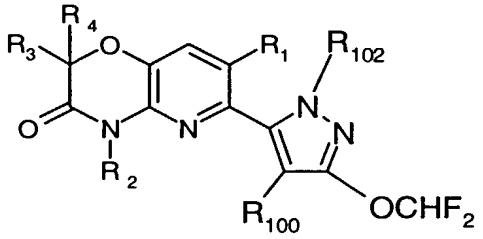
$$R_{102}\text{-}L_{10} \qquad \text{(XVI)},$$

wherein R_{102} is as defined for formula I with the exception of R_{102} as hydrogen, and L_{10} is a leaving group, for example halogen, especially chlorine, bromine or iodine, or sulfonate, especially mesyloxy or tosyloxy, in addition to the compound of formula IW_{100z}, wherein R_{102} is as defined, also yields the isomeric pyrazolone derivative of formula IW_{101z}



(IW_{101z}) ,

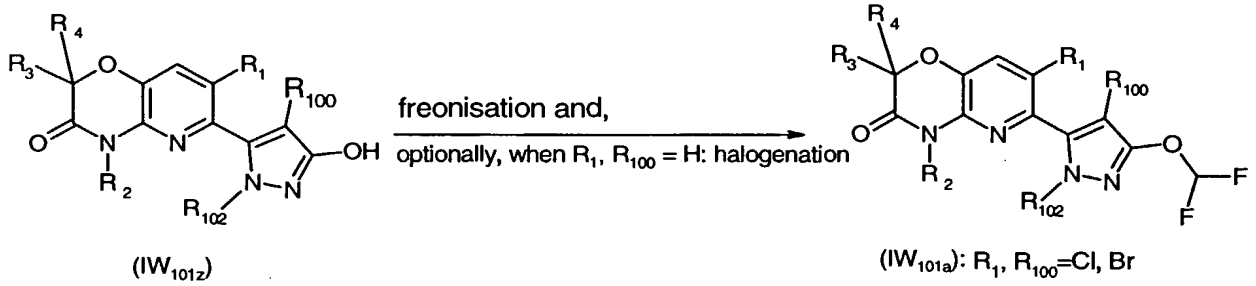
and, by means of a freonisation reaction, and when R_{100} is hydrogen optionally by means of a halogenation reaction, the corresponding isomeric compound of formula IW_{101a}



(IW_{101a})

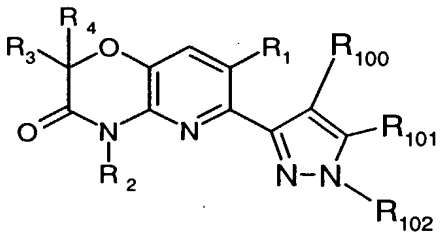
(Reaction Scheme 12). That compound may optionally be further functionalised according to the definitions of R_1, R_2, R_{100} and R_{102} for formula I by means of standard methods.

Reaction Scheme 12:



(IW_{101z}) (IW_{101a}): R_1, R_{100}=Cl, Br

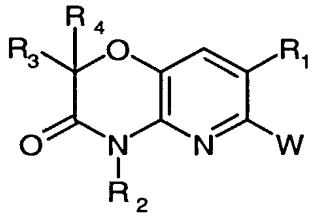
Further synthesis processes for the preparation of compounds of formula IW_{100}



(IW_{100}) ,

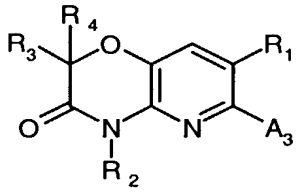
wherein R_1, R_2, R_3, R_4, R_{100} and R_{102} are as defined for formula I and R_{101} is trifluoromethyl (compound of formula IW_{100b}), cyano (compound of formula IW_{100c}), or methylthio, methylsulfinyl or methylsulfonyl (compound of formula IW_{100d}), or R_{101} and R_{102} together form a C_3-C_5alkylene bridge (compound of formula IW_{100e}), may be carried out in analogous manner to that described, for example, in WO 98/21199 and EP-A-0 839 808.

The process according to the invention for the preparation of compounds of formula I according to variant e) and Reaction Scheme 1e is carried out analogously to known processes and comprises, for the preparation of those compounds of formula I



(I)

wherein R_1, R_2, R_3, R_4 and W are as defined for formula I, reacting a compound of formula IIv



(IIv) ,

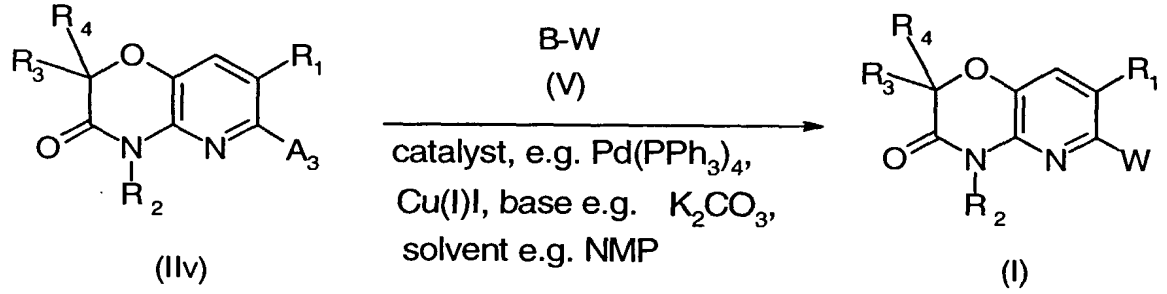
wherein R_1, R_2, R_3 and R_4 are as defined and A_3 either is a leaving group, for example halogen, especially chlorine or bromine, or sulfonate, especially trifluoromethylsulfonyloxy, or is a trialkylstannyl or boronic acid group, with a corresponding heterocyclic compound of formula V

B-W (V),

wherein W is as defined for formula I and B, complementarily to A_3 in the compound of formula IIv, either is a trialkylstannyl or boronic acid group or is a leaving group, for example halogen, especially chlorine or bromine, or sulfonate, especially trifluoromethylsulfonyloxy, in the presence of a metal catalyst from the noble metals group that is suitable for C-N or C-

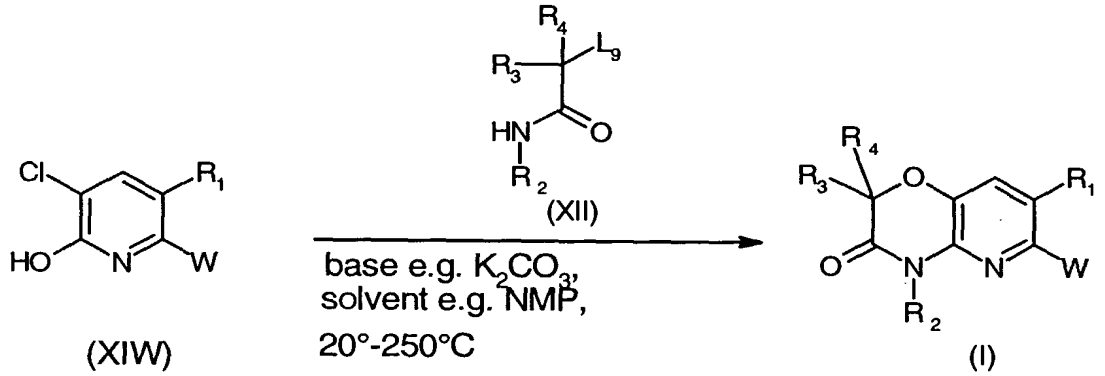
C linkages for example palladium, in the presence of a suitable activation ligand, for example triphenylphosphine or 2-(di-tert-butyl)diphenylphosphine, in the presence of a copper salt, for example copper iodide, in the presence of a suitable base, for example a trialkylamine, especially triethylamine, or a carbonate, especially sodium or potassium carbonate, and in a suitable solvent, for example N-methylpyrrolidone (NMP) or N,N-dimethylformamide (DMF) (Reaction Scheme 1e).

Reaction Scheme 1e:

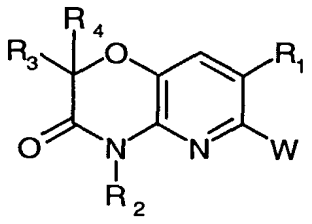


The process according to the invention for the preparation of compounds of formula I according to variant f) and Reaction Scheme 1f

Reaction Scheme 1f:

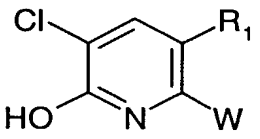


is carried out analogously to known processes and comprises, for the preparation of those compounds of formula I



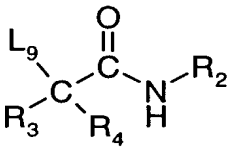
(I)

wherein R_1, R_2, R_3, R_4 and W are as defined for formula I, but W is especially a group W_{100}, reacting a compound of formula XIW



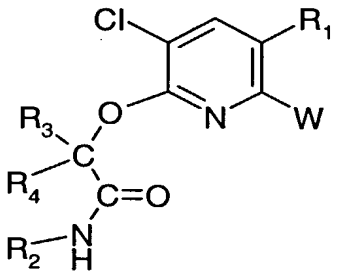
(XIW),

wherein R_1 and W are as defined for formula I, but W is especially a group W_{100} (compound of formula XIW_{100} in Reaction Scheme 22), in the presence of a base, for example a carbonate, especially sodium or potassium carbonate, and an inert organic solvent, for example N-methylpyrrolidone, at temperatures of from -20° to 250°C and normal pressure or under slight overpressure, but preferably at the boiling point of the solvent in question, with a compound of formula XII



(XII),

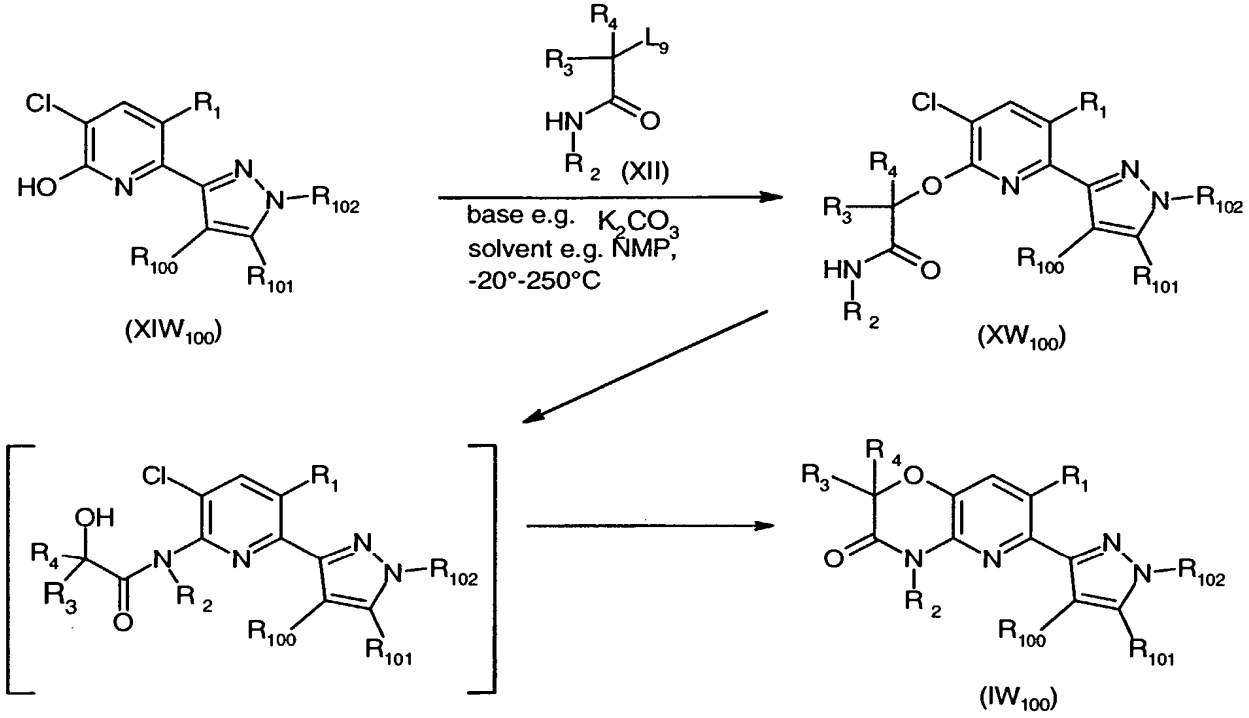
wherein R_2, R_3 and R_4 are as defined for formula I, and L_9 is a leaving group, for example halogen, especially chlorine or bromine, or sulfonate, especially mesyloxy, tosyloxy or trifluoromethanesulfonyloxy, to yield the compound of formula XW



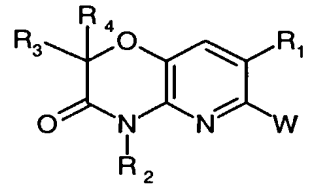
(XW)

and rearranging and cyclising that compound in the presence of base, for example a carbonate, especially sodium or potassium carbonate, and an inert organic solvent, for example an amide, e.g. N-methylpyrrolidone, at temperatures of from 20° to 250°C and under normal pressure or under slight overpressure but preferably at the boiling point of the solvent used. The above reaction sequence consisting of nucleophilic substitution, subsequent rearrangement and ring-closure reaction may proceed in the same reaction vessel, as a so-called 'one-pot reaction', as illustrated in Reaction Scheme 22.

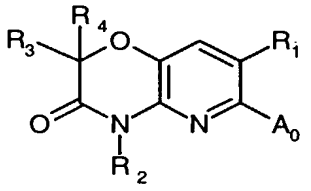
Reaction Scheme 22:



The process according to the invention for the preparation of compounds of formula I according to variant g) and Reaction Scheme 1g is carried out analogously to known processes, as described, for example, in Acta Chimica Scandinavica 23, 2322 (1969), and comprises, for the preparation of those compounds of formula I or IIz

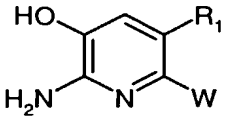


(I) or



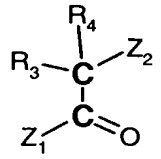
(IIz)

wherein R_1, R_3 and R_4 are as defined for formula I, R_2 is especially hydrogen, W is especially a group W_{14} or W_{100}-W_{109}, and A_0 is especially hydrogen, methyl, ethyl, fluorine, chlorine, bromine or carboxy, condensing a compound of formula XXIX



(XXIX) ,

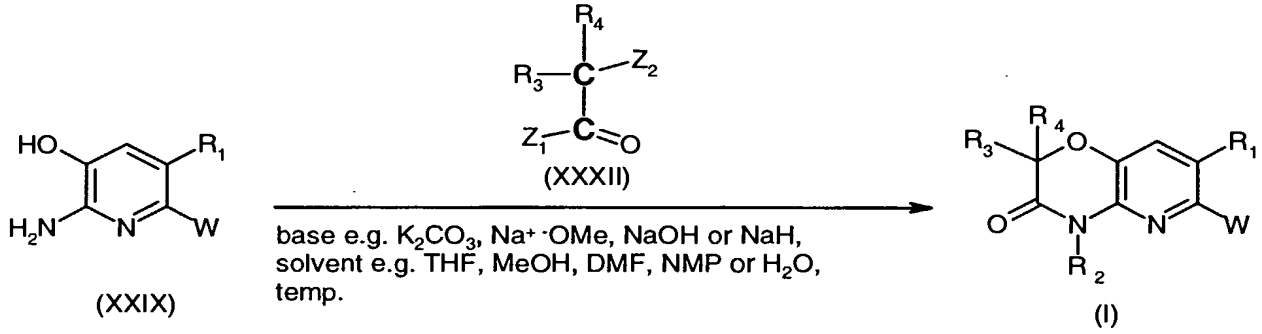
wherein R_1 and W are as defined, with an acetic acid derivative of formula XXXII



(XXXII) ,

wherein R_3 and R_4 are as defined, Z_1 is a C_1-C_4alkoxy group or a leaving group, for example chlorine or bromine, and Z_2 is a leaving group, for example chlorine or bromine, or a sulfonate, for example mesyloxy or tosyloxy, in the presence of a suitable base, for example an alkali metal carbonate, e.g. potassium carbonate, an alcoholate, e.g. sodium methanolate or potassium tert-butanolate, a hydride, e.g. sodium hydride, or a hydroxide, e.g. sodium, potassium or barium hydroxide, and a suitable solvent, for example an alcohol, e.g. methanol, ethanol or methyl Cellosolve, an ether, e.g. tetrahydrofuran, diethoxymethane or dioxane, an aromatic hydrocarbon, e.g. toluene, a nitrile, e.g. acetonitrile, an amide, e.g. DMF or NMP, a sulfoxide, e.g. dimethyl sulfoxide, or water.

Reaction Scheme 1g:



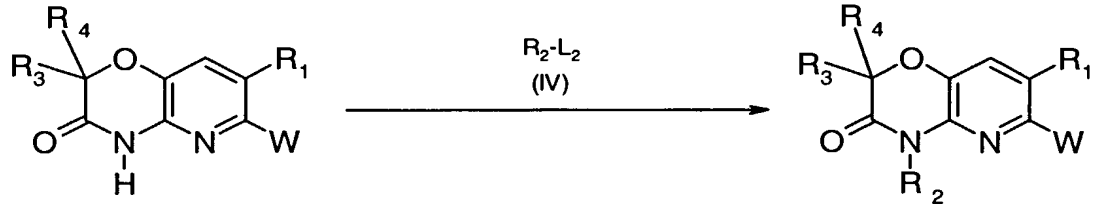
The process according to the invention for the preparation of compounds of formula I comprises, in accordance with

variant a), reacting compounds of formula Ia, wherein R_1, R_3, R_4 and W are as defined for formula I, with an appropriate alkylating reagent of formula IV

$$R_2\text{-}L_2 \quad (IV),$$

wherein R_2 is as defined for formula I with the exception of R_2 as hydrogen, and L_2 is a leaving group, in the presence of a base and a suitable solvent, as illustrated in Reaction Scheme $1a_0$:

Reaction Scheme $1a_0$:

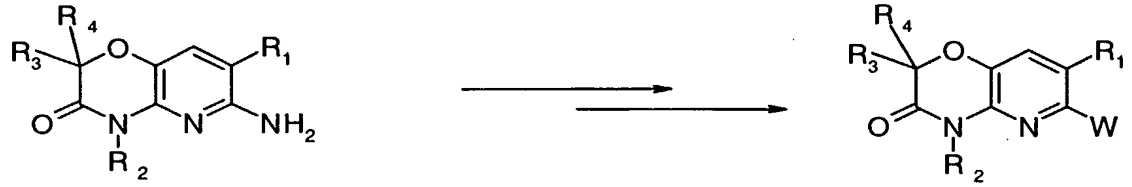


(Ia) (I): $W=W_1$-W_{10}, W_{100}-W_{108}

or

variant b), converting compounds of formula IIa, wherein R_1 to R_4 are as defined for formula I, analogously to known one- or multi-stage synthesis processes, into the corresponding cyclic ring systems W_1 to W_{10} or W_{100} to W_{108} in a multi-stage synthesis according to Reaction Scheme $1b_0$:

Reaction Scheme $1b_0$:

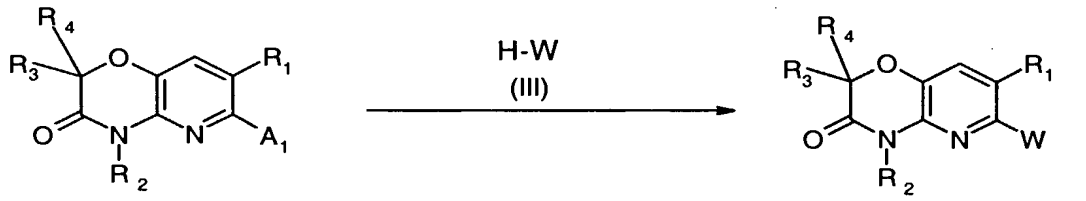


(IIa) (I): $W=W_1$-W_{10}, W_{100}-W_{108}

or

variant c), reacting compounds of formula IIb, wherein R_1 to R_4 are as defined for formula I and A_1 is a leaving group, for example fluorine, chlorine, bromine, methylsulfonyl, trifluoromethylsulfonyloxy, methylsulfonyloxy, phenylsulfonyloxy or nitro, in the presence of a base and one or more suitable catalysts and a suitable diluent, with a cyclic compound of formula III, wherein W is as defined for formula I, according to Reaction Scheme $1c_0$:

Reaction Scheme $1c_0$:



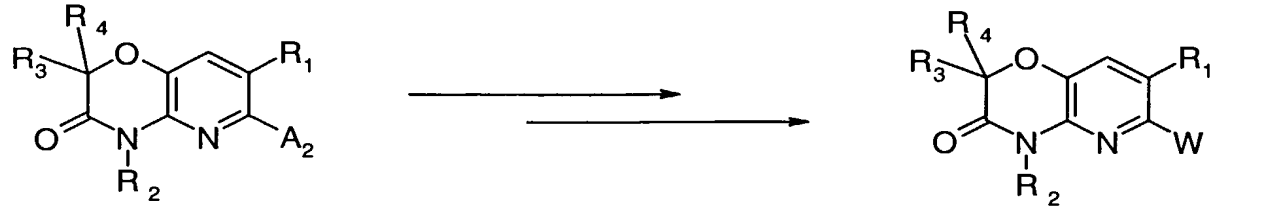
(IIb) (I): $W=W_1$-W_{10}, W_{100}-W_{108}

or

variant d), converting compounds of formula IIu, wherein R_1 to R_4 are as defined for formula I and A_2 is methyl, cyano, formyl, acyl, carboxyl or C_1-C_4alkoxycarbonyl, analogously to known one- or multi-stage synthesis processes, according to Reaction

Scheme 1d_0, into the corresponding cyclic C-C-linked ring systems of formula I wherein W is W_{100} to W_{108}:

Reaction Scheme 1d_0:



(IIu) (I): $W=W_{100}$-W_{108}

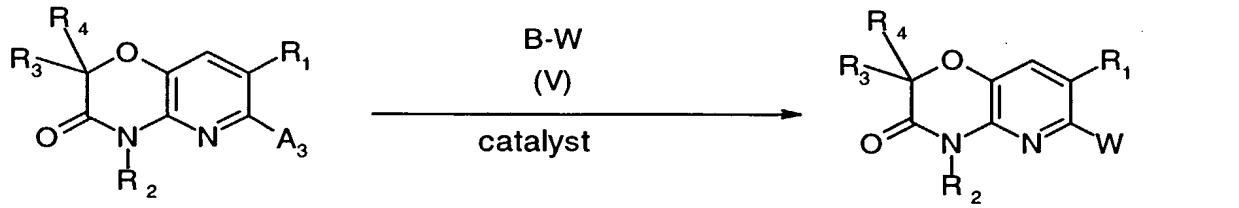
or

variant e), reacting compounds of formula IIv, wherein R_1 to R_4 are as defined for formula I and A_3 either is a leaving group, for example chlorine, bromine or trifluoromethylsulfonyloxy or is a trialkylstannyl or boronic acid group, with a corresponding heterocyclic compound of formula V

B-W (V),

wherein W is as defined above for W_1 to W_{10} or W_{100} to W_{108}, and B, complementarily to A_3, either is a trialkylstannyl or boronic acid group, or is a leaving group, for example chlorine, bromine or trifluoromethylsulfonyloxy, in the presence of a metal catalyst from the noble metals group that is suitable for C-N or C-C linkages, for example palladium, in the presence of a suitable activation ligand, for example triphenylphosphine or 2-(di-tert-butyl)diphenylphosphine, in the presence of a copper salt, for example copper iodide, and in the presence of a suitable base, for example potassium carbonate or triethylamine, in a suitable inert solvent, for example N-methylpyrrolidone or dimethylformamide, according to Reaction Scheme 1e_0:

Reaction Scheme 1e_0:



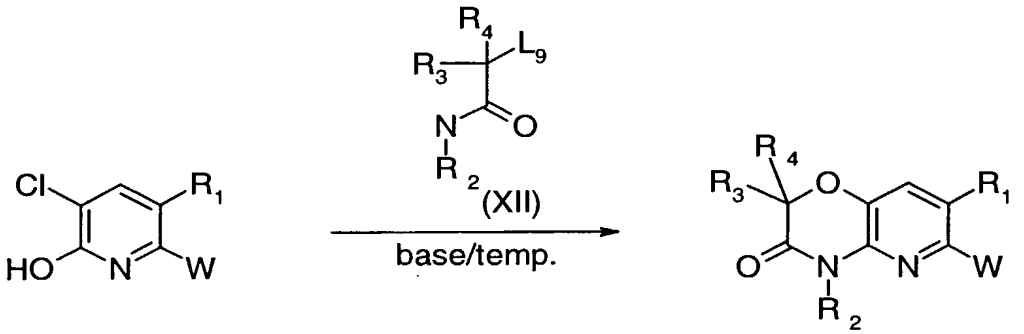
(IIv) (I): W_1-W_{10}, W_{100}-W_{108}

or

variant f), reacting compounds of formula XIW, wherein R_1 is as defined for formula I, and W is especially a group W_{100}, in the presence of a base and an inert solvent at elevated

temperatures, with a compound of formula XII, wherein R_2 to R_4 are as defined for formula I and L_9 is a leaving group, as illustrated in Reaction Scheme $1f_0$:

Reaction Scheme $1f_0$:



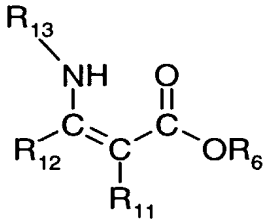
(XIW)

(I): $W=W_{100}$-W_{108}

The process according to the invention described under variant b) and in Reaction Scheme 1b for the preparation of compounds of formula I wherein W is a group W_1 is carried out analogously to known processes, as described, for example, in WO 99/52892 and WO 98/27083, and comprises converting a compound of formula IIa (Reaction Scheme 1_0), using a suitable reagent, for example oxalyl chloride, phosgene or thiophosgene, or using a reagent of formula VI_0

$$Cl\text{-}C(X_2)OR_5 \qquad (VI_0),$$

wherein X_2 is as defined for formula I and R_5 is C_1-C_4alkyl, into an intermediate of formula IId or IIc_0, respectively, and then condensing that intermediate with the corresponding enamine of formula VIIb



(VIIb),

wherein R_{11}, R_{12} and R_{13} are as defined for formula I and R_6 is C_1-C_4alkyl, in the presence of from 0.1 to 1.5 equivalents of a suitable base in an inert solvent to form the group W_1 and then, optionally, in an additional standard conversion reaction, either

aa) when X_1 and/or X_2 are sulfur, treatment with a thionating reagent, for example Lawesson's reagent, is carried out, or

ab) when R_{13} is hydrogen and X_2 is oxygen, reaction with an alkylating reagent of formula IX

$$R_{13}\text{-}L_1 \qquad \text{(IX)},$$

wherein R_{13} is as defined above with the exception of R_{13} as hydrogen, and L_1 is a leaving group, is carried out, and/or

ac) when R_2 is hydrogen, reaction, according to process variant a), with an appropriate alkylating reagent of formula IV

$$R_2\text{-}L_2 \qquad \text{(IV)},$$

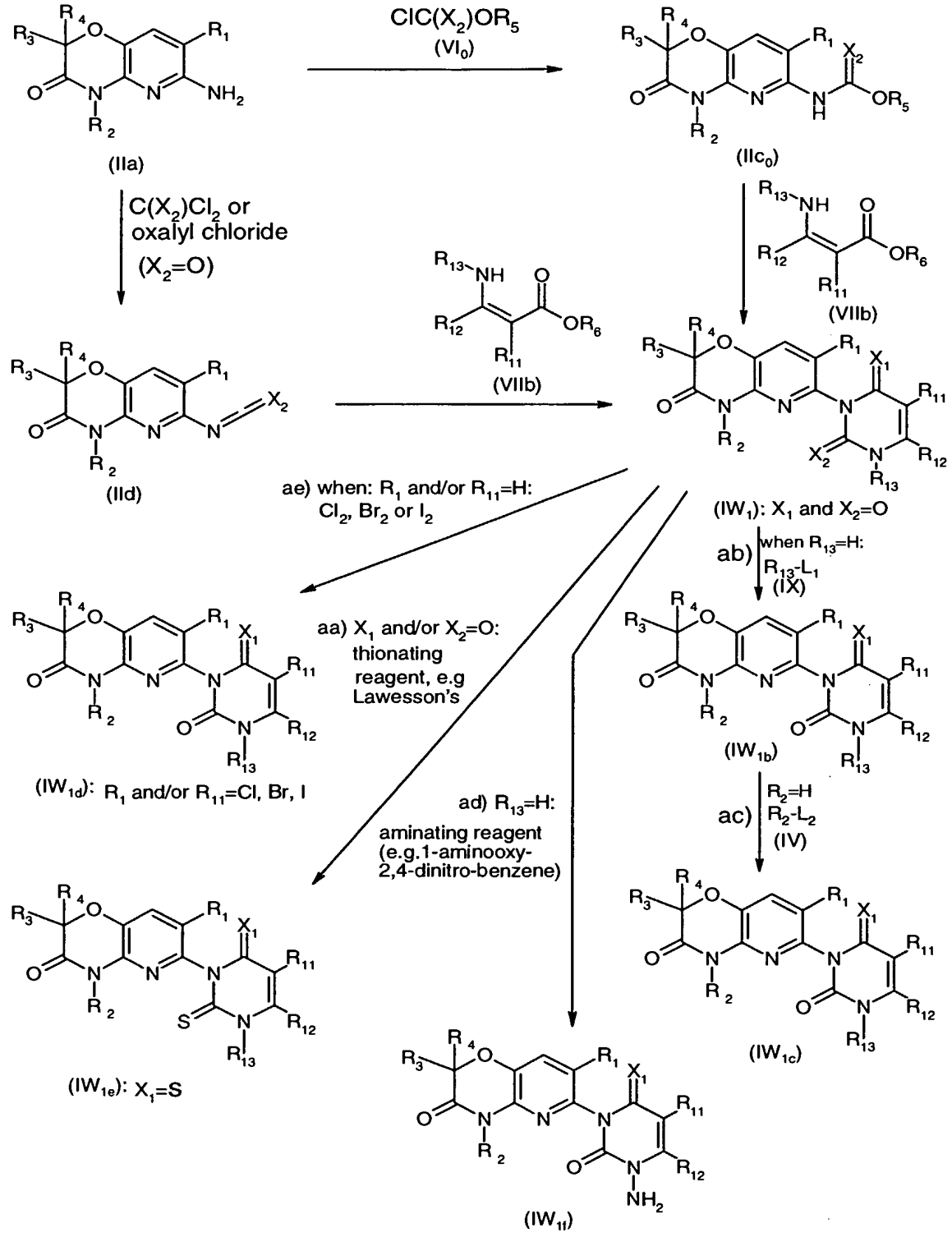
wherein R_2 is as defined for formula I with the exception of R_2 as hydrogen, and L_2 is a leaving group, for example chlorine, bromine, methylsulfonyloxy or phenylsulfonyloxy, is carried out, and/or

ad) when R_{13} is amino, treatment with an electrophilic aminating agent, as described, for example, in WO 96/36614, is carried out, and/or

ae) when R_1 and/or R_{11} are chlorine, bromine or iodine, treatment with a corresponding halogenating reagent is carried out.

Those synthesis sequences are illustrated in Reaction Scheme 1_0.

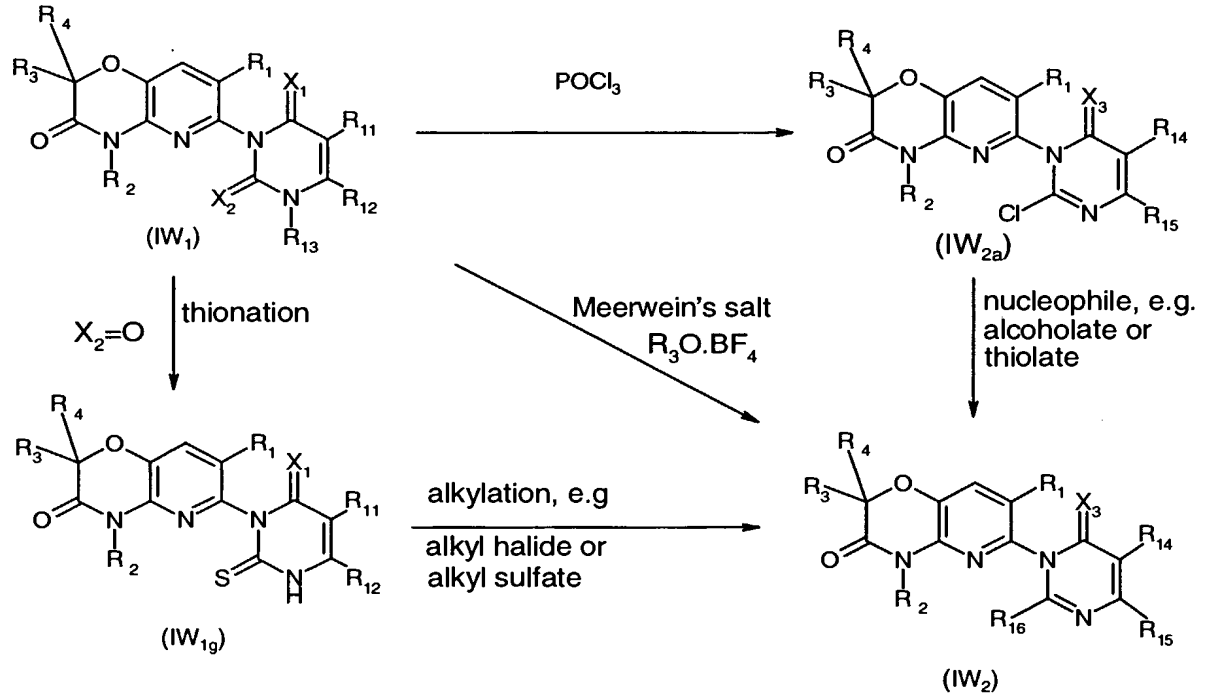
Reaction Scheme 1_0:



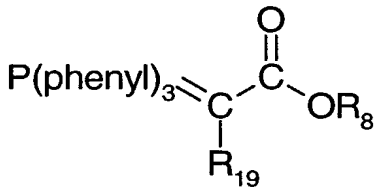
Compounds of formula I wherein W is a group W_2 can be obtained under particular conversion conditions from compounds of formula IW_1 wherein R_{13} is hydrogen and X_2 is

oxygen or sulfur, either using an alkylating reagent or using a chlorinating reagent and a subsequent substitution reaction. Reaction Scheme 2_0 illustrates that process.

Reaction Scheme 2_0:



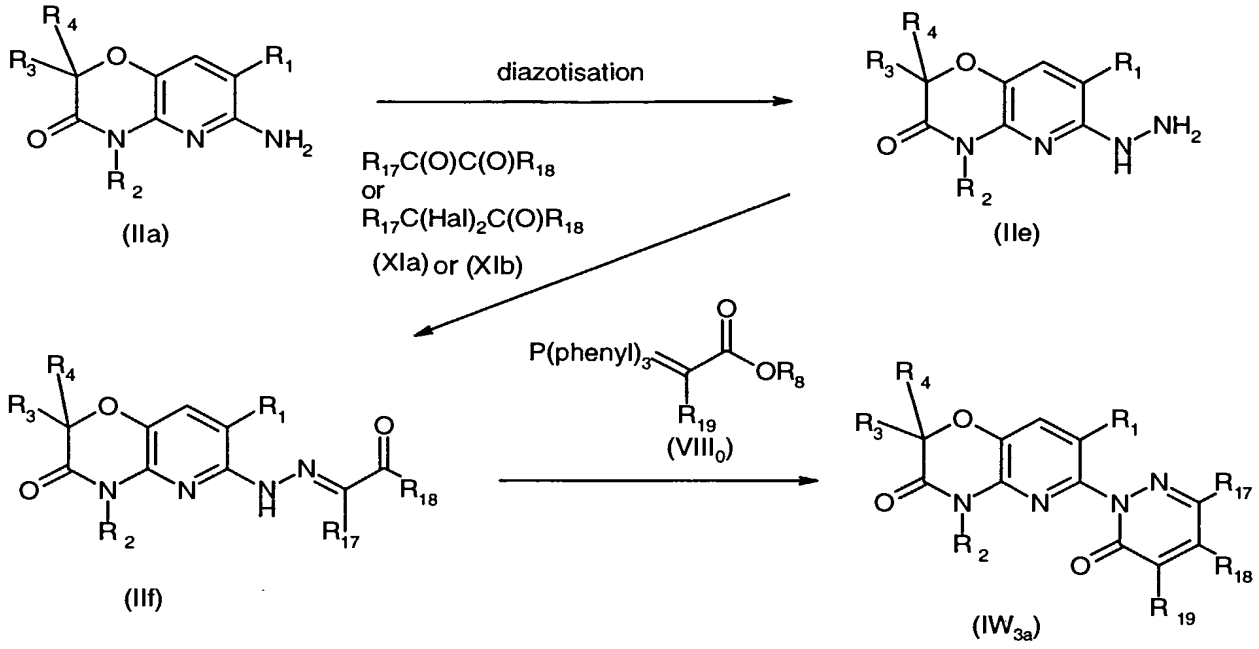
The process according to the invention described under variant b) for the preparation of compounds of formula I wherein W is a group W_3 is likewise carried out analogously to known processes and comprises first of all converting a compound of formula IIa, under diazotisation and condensation conditions, *via* a hydrazine derivative of formula IIe into a hydrazone of formula IIf, wherein R_{17} and R_{18} are as defined for formula I, and then condensing that hydrazone with a Wittig reagent of formula $VIII_0$



($VIII_0$),

wherein R_{19} is as defined for formula I and R_8 is C_1-C_4alkyl, in the presence of from 0.1 to 1.5 equivalents of a suitable base in an inert solvent to form the cyclic group W_3, and then, optionally, further reacting in an additional conversion reaction according to the corresponding meanings of R_1, R_2, R_{18} and X_5 in analogous manner to that described under aa), ac) or ae). Reaction Scheme 3_0 illustrates that reaction sequence.

Reaction Scheme 3_0:

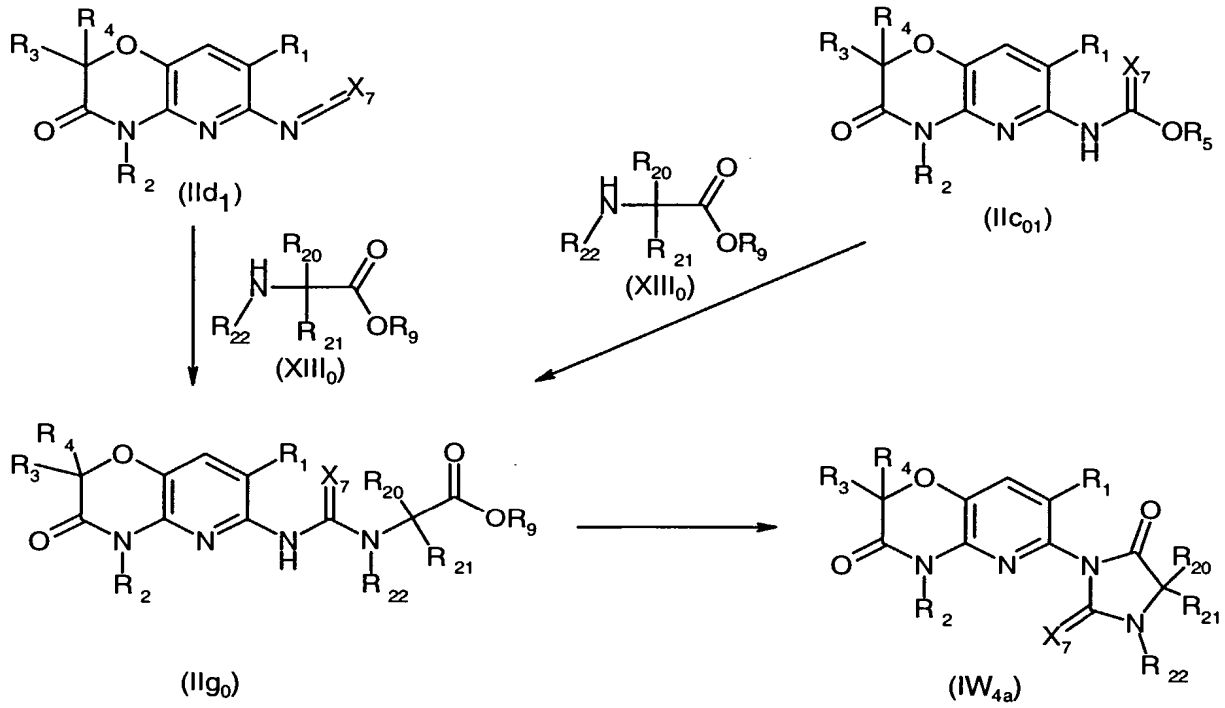


The process according to the invention described under variant b) for the preparation of compounds of formula I wherein W is a group W_4 is likewise carried out analogously to known processes, as described, for example, in EP-A-0 272 594, EP-A-0 493 323, DE-A-3 643 748, WO 95/23509, US-A-5 665 681 and US-A-5 661 109, and comprises reacting a compound of formula IIc_{01} or IId_1 with an amino acid ester of formula $XIII_0$, wherein R_{20} , R_{21} and R_{22} are as defined for formula I and R_9 is C_1-C_4alkyl, and condensing the resulting intermediate of formula IIg_0 to form the cyclic group of formula W_{4a} and then, optionally, further reacting the resulting compound in an additional conversion reaction according to the corresponding meanings of R_1, R_2, R_{20}, R_{21} and X_7 as described under aa), ac) or ae) or, when R_{22} is hydrogen, further reacting the resulting compound with an appropriate alkylating agent of formula X

$$R_{22}\text{-}L_5 \qquad (X),$$

wherein R_{22} is C_1-C_3alkyl and L_5 is a leaving group, for example halogen, especially chlorine, bromine or iodine, in the presence of a base. Reaction Scheme 4_0 illustrates that reaction sequence.

Reaction Scheme 4_0:

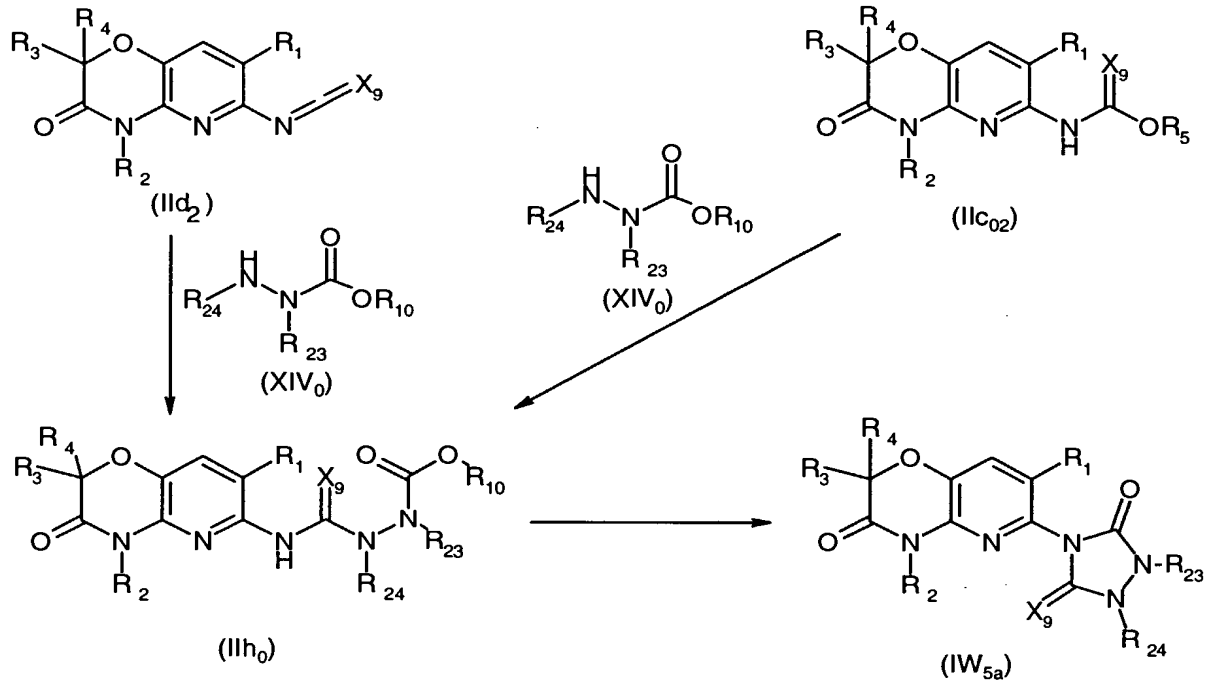


The process according to the invention described under variant b) for the preparation of compounds of formula I wherein W is a group W_5 is carried out analogously to known processes, as described, for example, in EP-A-0 210 137, DE-A-2 526 358, EP-A-0 075 267 and EP-A-0 370 955, and comprises reacting a compound of formula IIc_{02} or IId_2 with a hydrazide ester of formula XIV_0, wherein R_{23} and R_{24} are as defined for formula I and R_{10} is C_1-C_4alkyl, in the presence of a base and a suitable solvent, and then condensing the intermediate of formula IIh_0 to form the cyclic group of formula W_{5a} and then, optionally, further reacting the resulting compound in an additional conversion reaction according to the corresponding meanings of R_1, R_2, R_{23}, R_{24} and X_9 in analogous manner to that described under aa), ac) or ae) or, when R_{23} and/or R_{24} are hydrogen, further reacting the resulting compound with an appropriate alkylating agent of formula XVa and/or XVb

R_{23}-L_3 (XVa) and/or R_{24}-L_4 (XVb),

wherein R_{23} and R_{24} are as defined for formula I with the exception of R_{23} and R_{24} as hydrogen, and L_3 and L_4 are leaving groups, for example halogen, especially chlorine, bromine or iodine, in the presence of a base. Reaction Scheme 5_0 illustrates that reaction sequence.

Reaction Scheme 5_0:



In analogous manner, compounds of formula I wherein W is a group W_6, W_7, W_8, W_9 or W_{10} can also be prepared in accordance with the processes according to the invention described under variant b).

In process variant c), suitable catalysts are especially metal catalysts, for example $Pd(PPh_3)_4$, $Pd(PPh_3)Cl_2$, $Pd(OAc)_2$ and copper iodide. Further suitable catalytic additives include various phosphine ligands, for example biphenyl-2-bis-tert-butylphosphine, and various bases, for example triethylamine, potassium carbonate and caesium fluoride.

The process according to the invention described under variant d) for the preparation of compounds of formula I wherein W is, for example, a group W_{100}, R_{101} is difluoromethoxy, R_{102} is hydrogen, chlorine or bromine and R_1, R_2, R_3, R_4 and R_{100} are as defined for formula I, is likewise carried out analogously to known synthesis processes, as described, for example, in EP-A-0 839 808 and WO 98/21199, and comprises converting a carboxylic acid of formula IIu_1, *via* its acid chloride of formula IIu_2, using a suitable malonic acid ester of formula XL_0

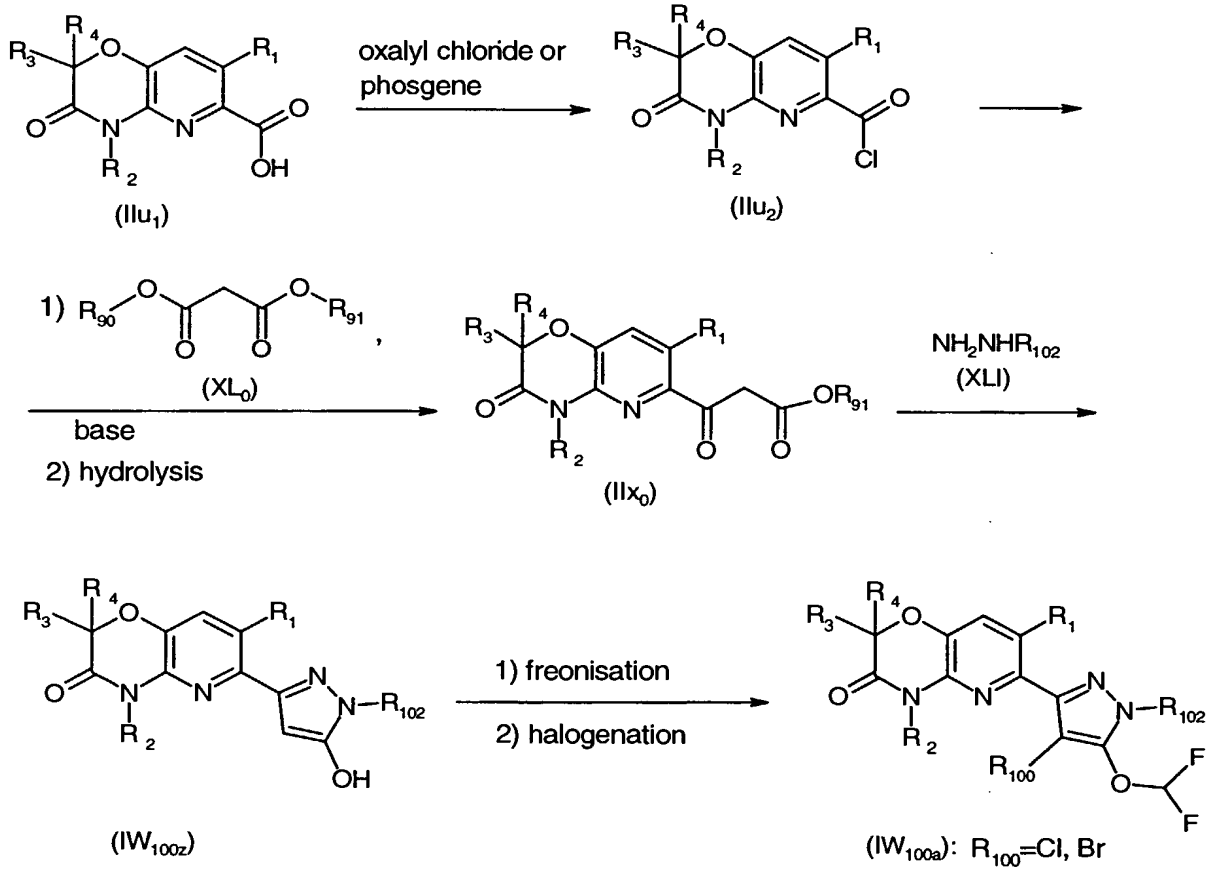
$$R_{90}OC(O)CH_2C(O)OR_{91} \qquad (XL_0),$$

wherein R_{90} is hydrogen, trimethylsilyl or C_1-C_4alkyl and R_{91} is C_1-C_4alkyl, in the presence of a suitable base and an inert solvent, into the keto ester of formula IIx_0, and then cyclising that keto ester with a corresponding hydrazine derivative of formula XLI

$$H_2NNHR_{102} \qquad (XLI),$$

wherein R_{102} is as defined for formula I, to form a pyrazolone derivative of formula IW_{100z}, which is then subjected to freonisation and subsequently to a halogenation reaction. In the first stage therein, instead of R_{90} as hydrogen, a sodium, potassium or magnesium salt of the malonic acid monoalkyl ester may also be advantageously used. The freonisation is advantageously performed in the presence of a suitable base in water or in a two-phase system consisting of a chlorinated hydrocarbon and water or, optionally, advantageously in a closed system and under slight overpressure. Reaction Scheme 11_0 illustrates that reaction sequence for the preparation of compounds of formula IW_{100a}.

Reaction Scheme 11_0:



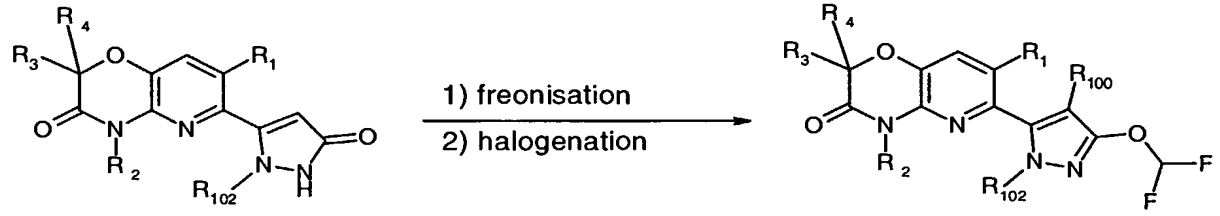
In further conversion reactions, in analogous manner to that described under ac) above, the compounds of formula IW_{100a} wherein R_1 and/or R_2 are hydrogen may be further reacted,

according to process variant a), with an appropriate alkylating reagent of formula IV R_2-L_2 (IV) or, as described under ae), with a corresponding halogenating reagent. If the halogenation reaction is performed in the presence of an excess of halogenating reagent, there are formed, from compounds of formula IW_{100z} wherein R_1 is hydrogen, compounds of formula IW_{100a} wherein both R_1 and R_{100} are accordingly simultaneously chlorine or bromine. When unsubstituted hydrazine of formula XLI wherein R_{102} is hydrogen is used, compounds of formula IW_{100z} are obtained wherein R_{102} is hydrogen. Those compounds can be reacted with an appropriate alkylating agent of formula XVI

$$R_{102}\text{-}L_{10} \qquad \text{(XVI)},$$

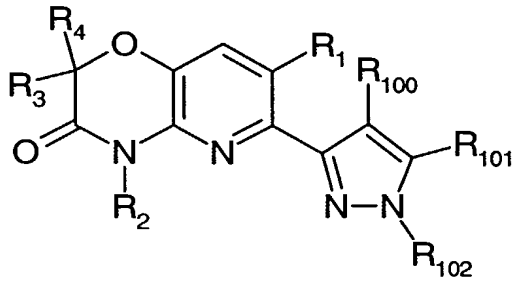
wherein R_{102} is as defined for formula I with the exception of R_{102} as hydrogen, and L_{10} is a leaving group, to form the corresponding compound of formula IW_{100a} wherein R_{102} is as defined. In addition, in that alkylation reaction there are also formed the isomeric compounds of formula IW_{101z}, which, after the freonisation reaction and, optionally, the halogenation reaction, form the corresponding isomeric compounds of formula IW_{101a}, as illustrated in Reaction Scheme 12_0.

Reaction Scheme 12_0:



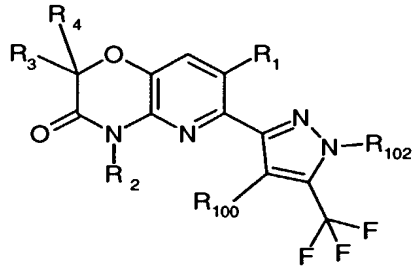
(IW_{101z}) (IW_{101a}): R_{100}=Cl, Br

Corresponding synthesis processes for the preparation of compounds of formula IW_{100}

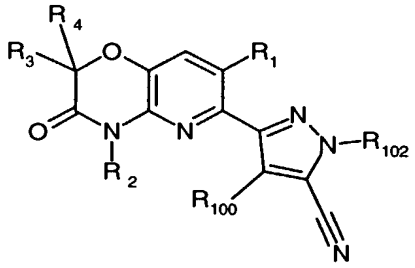


(IW_{100})

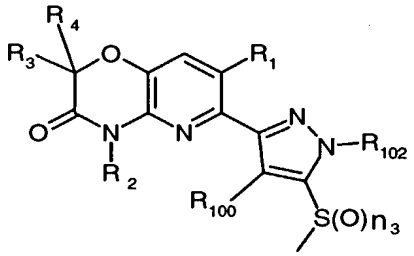
wherein R_{101} is trifluoromethyl (compounds of formula IW_{100b}), cyano (compounds of formula IW_{100c}), methylthio (n_3=0), methylsulfinyl (n_3=1) or methylsulfonyl (n_3=2) (compounds of formula IW_{100d}), or wherein R_{101} and R_{102} together form a C_3-C_5alkylene chain (n_4 = 0, 1 or 2) (compounds of formula IW_{100e}) are known, for example, from WO 98/21199 and EP-A-0 839 808.



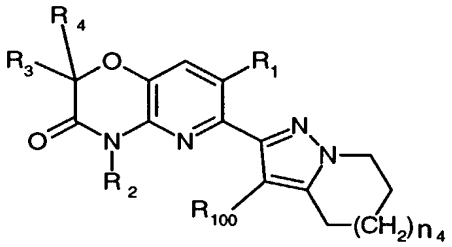
($IW_{100}b$),



(IW_{100c}),

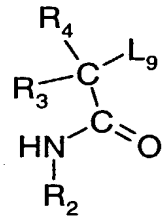


(IW_{100d}) and



(IW_{100e})

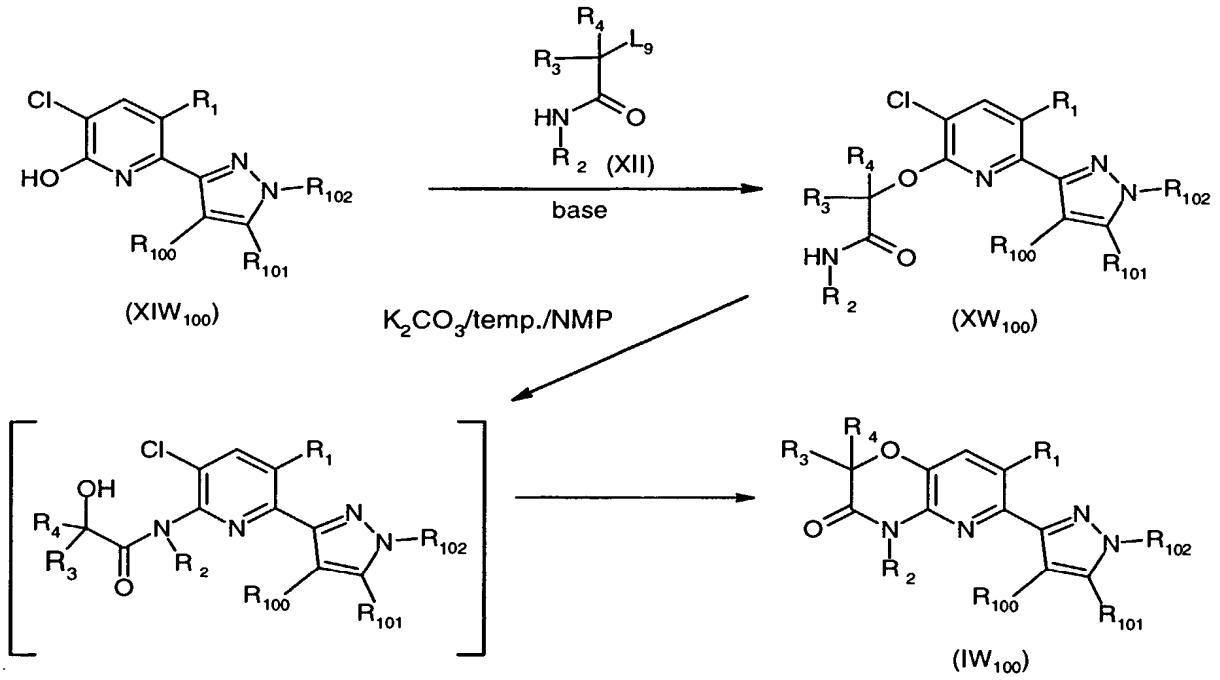
Compounds of formula IW_{100} may also be prepared according to process variant f) described above by reacting a compound of formula XIW_{100}, wherein R_1 and W are as defined for formula I, with a corresponding acetamide of formula XII



(XII),

wherein R_2, R_3 and R_4 are as defined for formula I and L_9 is a leaving group, for example chlorine, bromine, mesyloxy, tosyloxy or trifluoromethylsulfonyloxy, in the presence of a base and an inert solvent, for example N-methylpyrrolidone (NMP), at temperatures of from 20° to 250°C and at normal pressure or under slight overpressure, but preferably at the boiling point of the solvent in question. Reaction Scheme 22_0 illustrates that reaction sequence.

Reaction Scheme 22_0:



Compounds of formulae XW_{100} and XIW_{100} either are known or can be prepared analogously to the processes described in WO 98/42698.

Compounds of formula I wherein W is a group W_{103} (compounds of formula IW_{103}) can be prepared in analogous manner to that described in WO 99/06394 and WO 98/07720.

Compounds of formula I wherein W is a group W_{104} (compounds of formula IW_{104}) can be prepared in analogous manner to that described in WO 97/11060.

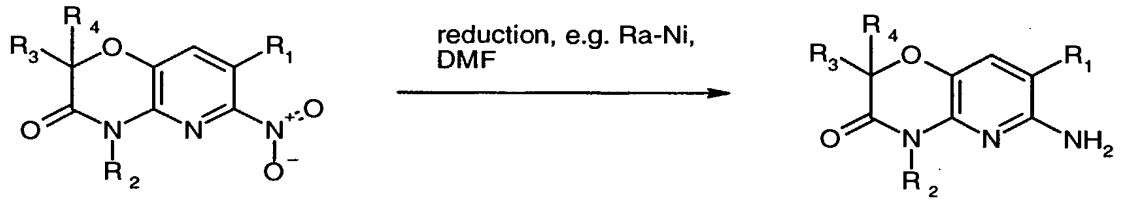
Compounds of formula I wherein W is a group W_{107} (compounds of formula IW_{107}), can be prepared in analogous manner to that described in WO 97/06150.

The resulting compounds of formula I and salts thereof can be isolated in customary manner by concentrating or evaporating off the solvent and can be purified by recrystallisation or trituration of the solid residue in solvents in which they are not readily soluble, for example ethers or aromatic or chlorinated hydrocarbons. Moreover, the person skilled in the art will be familiar with the sequence in which certain reactions among the process variants described should be advantageously performed in order to avoid possible undesired competing reactions.

Where synthesis is not directed at the isolation of pure isomers, the product may be in the form of a mixture of two or more isomers. The isomers can be separated according to methods known *per se*. If desired, pure optically active isomers can, for example, also be prepared by synthesis starting from corresponding optically active starting materials.

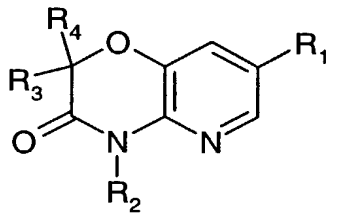
The 6-amino-4H-pyrido[3,2-b][1,4]oxazin-3-ones of formula IIa (Reaction Scheme 1b) used as starting compounds can be prepared by reducing 6-nitro-4H-pyrido[3,2-b][1,4]oxazin-3-one of formula IIn, wherein R_1, R_2, R_3 and R_4 are as defined for formula I, under known reaction conditions, for example using iron trichloride ($Fe(III)Cl_3$) in acetic acid according to Béchamps or in the presence of hydrogen and a metal catalyst, for example Raney nickel or palladium on activated carbon, in an inert diluent, for example an ether, especially tetrahydrofuran or dioxane, an alcohol, especially ethanol, an amide, especially N,N-dimethylformamide (DMF) or N-methylpyrrolidone (NMP) or water, as illustrated in Reaction Scheme 13.

Reaction Scheme 13:



(IIn) (IIa)

The 6-nitro-4H-pyrido[3,2-b][1,4]oxazin-3-ones of formula IIn used as starting compounds in Reaction Scheme 13 can be obtained selectively by means of aromatic nitration of compounds of formula XXX

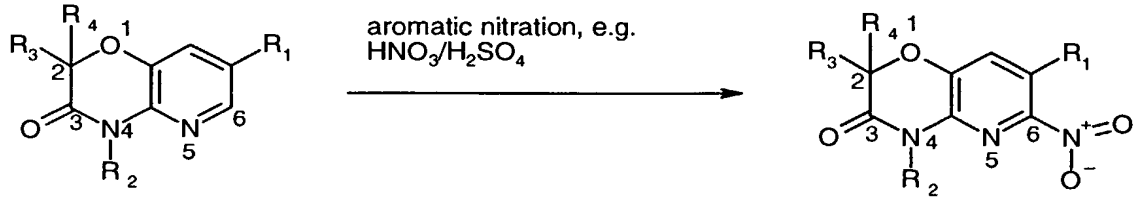


(XXX),

wherein R_1 to R_4 are as defined for formula I, under standard conditions, for example using HNO_3/H_2SO_4, as illustrated in Reaction Scheme 14, and then further functionalised according to the definitions of R_1 and R_2 for formula I in accordance with standard processes, for example alkylation and halogenation as described under ac) and ae). The aromatic nitration proceeds selectively in the 6-position of the 4-H-pyrido[1,4]oxazinone ring independently of the substituent R_1 (cf., in that respect, the analogous halogenation

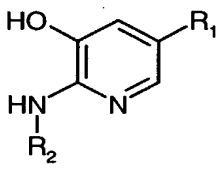
reaction, which, in contrast, takes place predominantly in the 7-position, e.g. US-A-3 854 926 and WO 88/08705).

Reaction Scheme 14



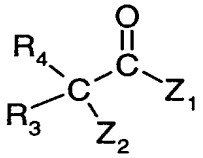
(XXX) (IIn)

The 4H-pyrido[3,2-b][1,4]oxazin-3-ones of formula XXX used as starting compounds in Reaction Scheme 14 can be obtained analogously to known processes, as described, for example, in Acta Chimica Scandinavica 23, 2322 (1969), from 2-amino-3-hydroxy-pyridine derivatives of formula XXXI



(XXXI),

wherein R_1 and R_2 are as defined for formula I, by reacting such a compound with a compound of formula XXXII

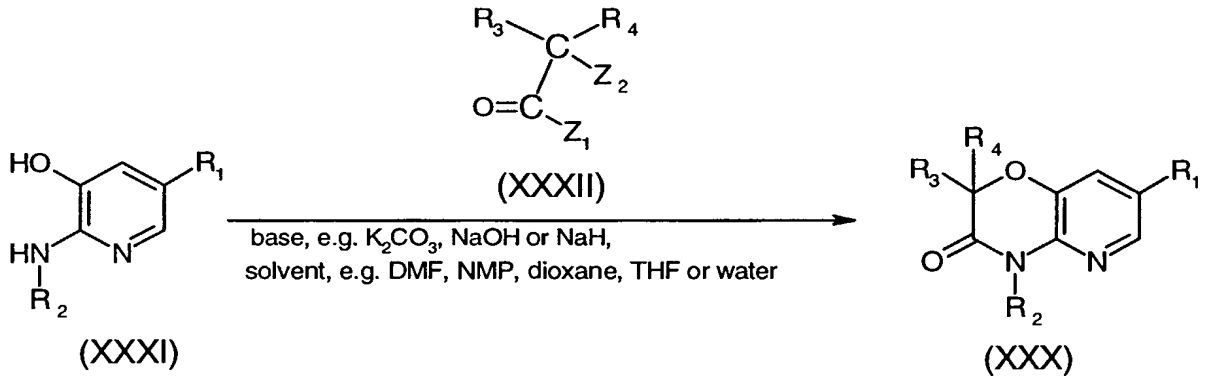


(XXXII),

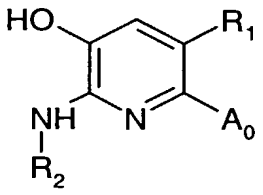
wherein R_3 and R_4 are as defined for formula I, Z_1 is a C_1-C_4alkoxy group, especially methoxy or ethoxy, or halogen, especially chlorine or bromine, and Z_2 is a leaving group, for example halogen, especially chlorine or bromine, or sulfonate, especially methylsulfonyloxy or phenylsulfonyloxy, in the presence of a suitable base, for example a carbonate, e.g. sodium or potassium carbonate, an alkali metal hydroxide, e.g. sodium or potassium hydroxide, or an alkali or alkaline earth metal hydride, e.g. sodium hydride, and in the presence of a suitable solvent, for example an ether, e.g. tetrahydrofuran or dioxane, an amide, e.g. DMF or NMP, or water, or a mixture of those solvents, as illustrated in Reaction Scheme 15. The compounds of formula XXX thereby obtained may then be further functionalised according to the definitions of R_1 and R_2 for formula I as described above, for

example, under ac) (alkylation using R_2-L_2 (IV)) and/or ae) (halogenation) and/or af) (fluorination).

Reaction Scheme 15:

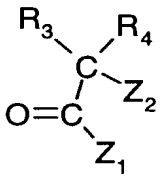


In analogous manner, for example, according to process variant g) and Reaction Scheme 15a, starting from a compound of formula XXVIII



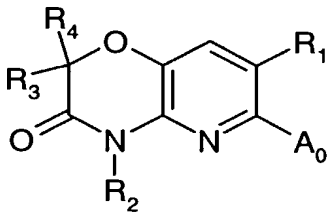
(XXVIII)

and a compound of formula XXXII



(XXXII),

it is also possible to prepare compounds of formula IIz

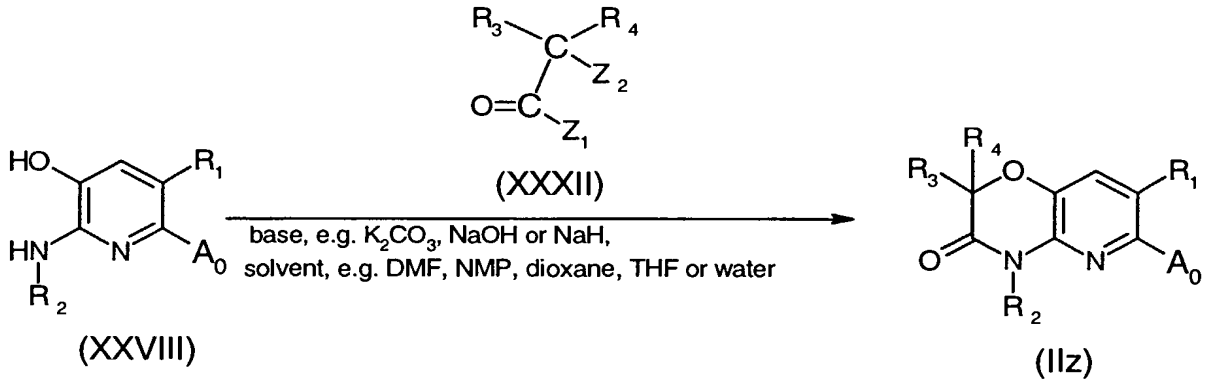


(IIz)

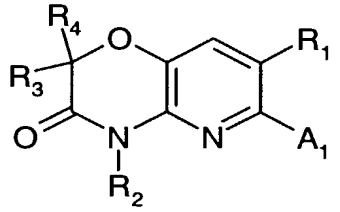
wherein in the compounds of formulae XXVIII, XXXII and IIz the substituents R_1, R_2, R_3 and R_4 are as defined for formula I, Z_1 is a C_1-C_4alkoxy group, especially methoxy or ethoxy, or halogen, especially chlorine or bromine, Z_2 is a leaving group, for example halogen, especially chlorine or bromine, or sulfonate, especially methylsulfonyloxy or

phenylsulfonyloxy, and A_0 is chlorine or bromine (= compounds of formula IIb) or, especially, methyl or carboxy (= compounds of formula IIu).

Reaction Scheme 15a:

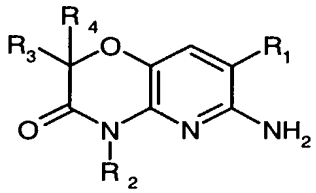


The starting compounds of formula IIb



(IIb),

wherein R_1 to R_4 are as defined for formula I and A_1 is halogen, C_1-C_4alkylthio, C_1-C_4alkylsulfonyl, C_1-C_4alkylsulfonyloxy, hydroxy or trifluoromethylsulfonyloxy, used for process variant c) above can be prepared, for example, from compounds of formula IIa

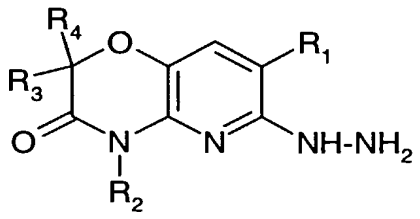


(IIa),

wherein R_1 to R_4 are as defined, by means of standard processes, for example diazotisation and boiling of the resulting diazonium salt (compound of formula IIee in Reaction Scheme 16b) to form the compound of formula IIb wherein A_1 is hydroxy, or by a Sandmeyer reaction of the resulting diazonium salt, for example using copper(I) chloride or copper(I) bromide, to form the compounds of formula IIb wherein A_1 is halogen, especially chlorine or bromine, and subsequently subjecting the hydroxy compound to treatment with C_1-C_4alkylsulfonic acid anhydride or trifluoromethanesulfonic acid anhydride to yield the compounds of formula IIb wherein A_1 is C_1-C_4alkylsulfonyloxy or trifluoromethylsulfonyloxy, or subsequently substituting the halogen compound of formula IIb (A = halogen) with C_1-C_4alkylthiolates to yield the compounds of formula IIb wherein A_1 is C_1-C_4alkylthio and then

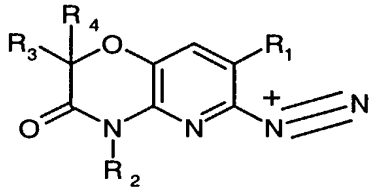
optionally converting those compounds by means of oxidation, for example using m-chloroperbenzoic acid or hydrogen peroxide in acetic acid, into the corresponding compounds of formula IIb wherein A_1 is C_1-C_4alkylsulfonyl.

The hydrazine derivatives of formula IIe



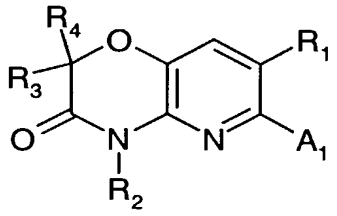
(IIe)

used in Reaction Schemes 3, 6, 6a and 10 can be obtained either by means of diazotisation of compounds of formula IIa, for example using sodium nitrite in hydrochloric acid or sulfuric acid, and reduction, for example using sodium sulfite or tin(II) chloride ($SnCl_2$), of the resulting diazonium salts of formula IIee



(IIee),

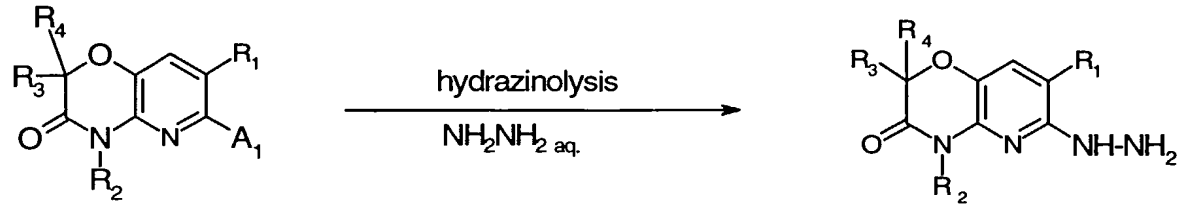
the substituents R_1 to R_4 in the compounds of formulae IIe and IIee being as defined for formula I, and M_1^- is an anion for example hydrogen sulfate or tetrafluoroborate, or halide, for example chloride, or by means of hydrazinolysis of the compounds of formula IIb



(IIb)

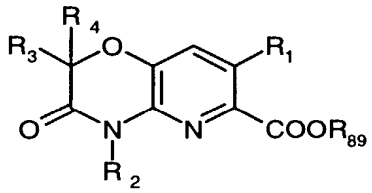
wherein R_1 to R_4 are as defined and A_1 is fluorine, chlorine, bromine or nitro, using hydrazine in water, ethanol or NMP, or in a mixture of those solvents, at temperatures of from 10° to 100°C, according to Reaction Scheme 15b.

Reaction Scheme 15b:



(IIb): A_1=F, Cl, Br, NO_2 (IIe)

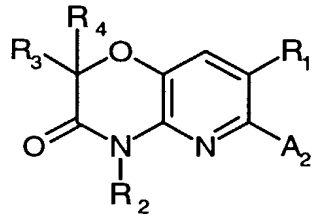
The starting compounds used for process variant d) above, 3-oxo-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazine-6-carboxylic acids or esters thereof of formula IIu_1



(IIu_1),

wherein R_1 to R_4 are as defined for formula I and R_{89} is hydrogen or C_1-C_4alkyl, can be prepared either

ba) by means of oxidation, using potassium permanganate, nitric acid or oxygen in the presence of a suitable metal catalyst, for example V_2O_5, Na_2WO_4, $Co(OAc)_3$ or $K_2Cr_2O_3$, starting from compounds of formula IIu



(IIu)

wherein R_1 to R_4 are as defined and A_2 is methyl (Reaction Scheme 16a), or

bb) by means of hydrolysis of compounds of formula IIu wherein R_1 to R_4 are as defined and A_2 is cyano, or

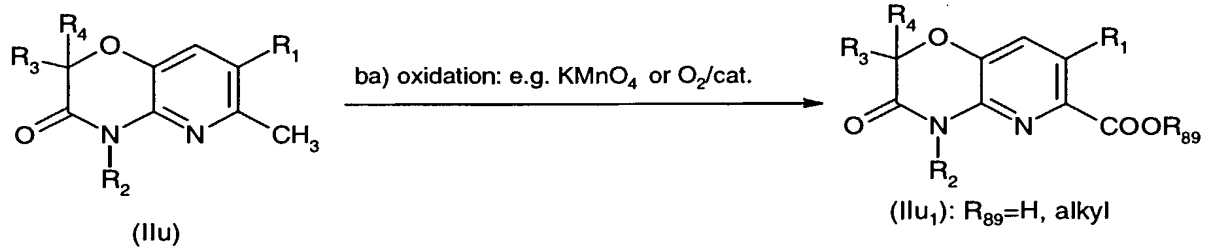
bc) by means of carbonylation of compounds of formula IIb wherein R_1 to R_4 are as defined and A_1 is chlorine or bromine, or

bd) by means of 1) diazotisation of the amines of formula IIa and 2) subsequent carbonylation of the diazonium salts of formula IIee obtained.

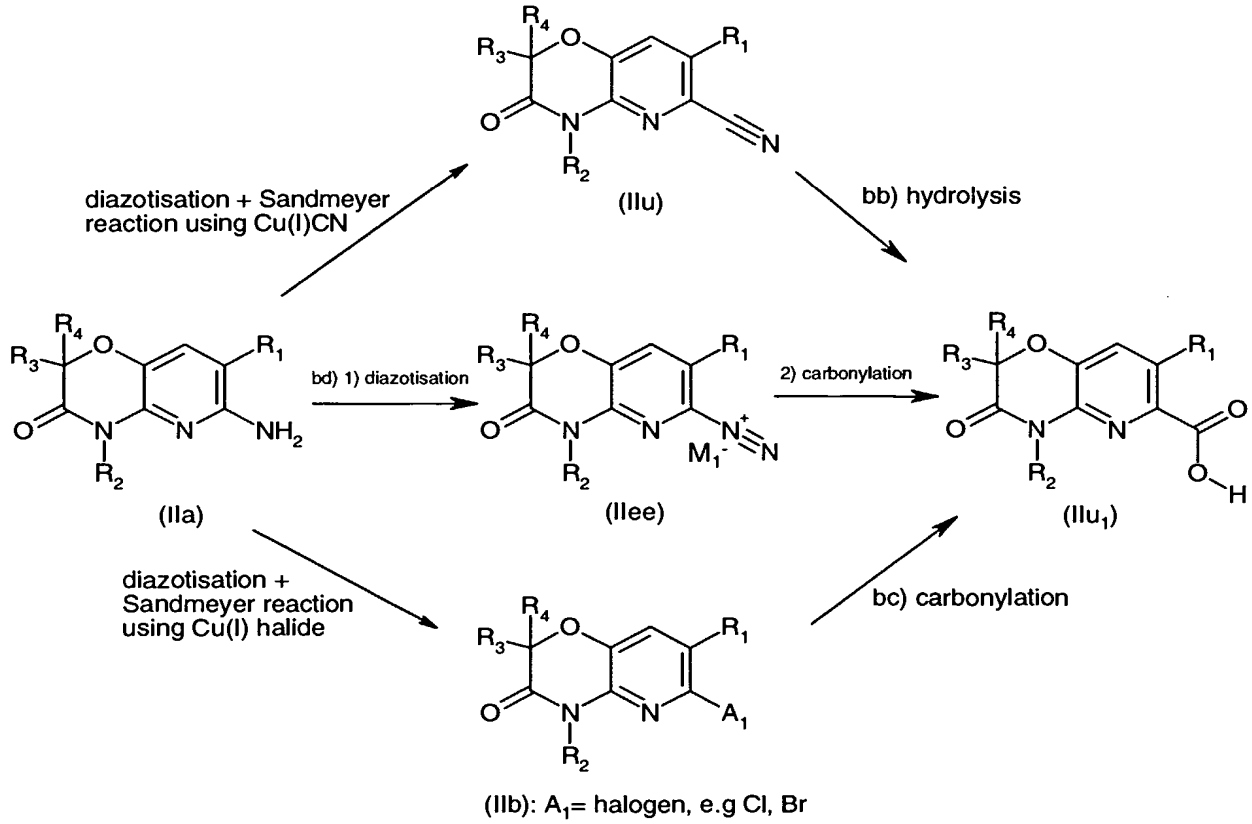
The cyano compounds of formula IIu used in process bb) can be obtained by means of diazotisation and a Sandmeyer reaction with addition of copper cyanide (Cu(I)CN).

Reaction Schemes 16a and 16b illustrate those conversions in diagrammatic form.

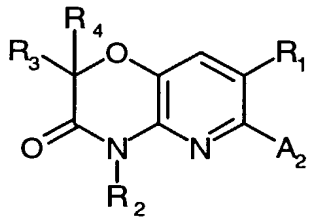
Reaction Scheme 16a:



Reaction Scheme 16b:

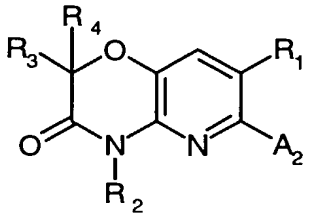


The starting compounds of formula IIu



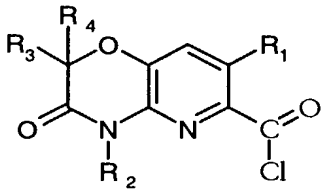
(IIu)

wherein R_1, R_2, R_3 and R_4 are as defined for formula I and A_2 is formyl or acyl, used in process variant d) can, for example, be prepared by standard methods, starting from compounds of formula IIu



(IIu)

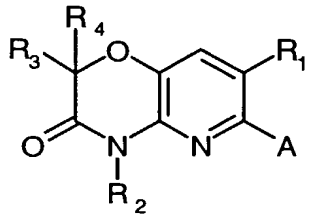
wherein R_1 to R_4 are as defined and A_2 is cyano, by means of reduction of the cyano group, for example using dibutylaluminium hydride (DIBAH), or starting from compounds of formula IIu_2



(IIu_2),

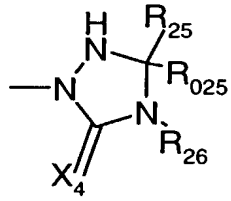
wherein R_1 to R_4 are as defined, by means of a Grignard reaction using methylmagnesium chloride, or using the reagent O,N-dimethyl acetamide.

The compounds of formula II



(II)

wherein R_1 to R_4 are as defined for formula I and A is fluorine, C_1-C_4alkylthio, C_1-C_4alkylsulfonyl, phenylthio, phenylsulfonyl, C_1-C_4alkylsulfonyloxy, trifluoromethylsulfonyloxy, hydroxy, nitro, amino, isocyanato, isothiocyanato, hydrazino, a group $NHC(X_2)X_0R_5$, $NHC(X_7)X_0R_5$, $NHC(X_8)X_0R_5$, $NHC(X_9)X_0R_5$, $NHC(X_3)R_{16}$, $NHN=C(R_{17})C(O)R_{18}$, $NHC(X_7)N(R_{22})C(R_{20})R_{21}C(X_6)OR_9$, $NHC(X_9)NR_{24}NR_{23}C(X_8)OR_{10}$, $NHC(X_8)NR_{23}NHR_{24}$, $NHN=C(R_{25})COOH$, $NHN=C(R_{25})R_{025}$, $N(C(X_4)\text{-}NHR_{26})N=CR_{25}R_{025}$, $N(C(X_4)NHR_{26})NH_2$, $NHN=C(R_{25})N(R_{26})C(X_4)OR_{84}$, $N(C(X_4)NHR_{26})NHC(O)OR_{84}$, $N(C(X_{19})NHR_{50})NHC(O)OR_{84}$, $NHC(X_{12})NHR_{26}$, $NHC(O)C(R_{28})=C(R_{27})C(O)OR_{85}$, $NHC(=NR_{39})NHR_{38}$, $NHC(Y_2)NR_{40}NHR_{41}$, $NHC(Y_2)NR_{40}NR_{41}C(O)OR_9$, $NHN=C(R_{42})C(O)NHR_{43}$, $NHN=C(R_{42})C(O)N(R_{43})C(O)OR_{85}$, $N(R_{43})COOR_{85}$, $NHC(R_{53})=NNHC(X_{21})OR_{85}$, $NHC(S)NHC(=NR_{57})R_{56}$, $NHC(X_{23})NHR_{58}C(X_{25})NHR_{59}$, $N(C(X_{24})NHR_{59})C(X_{23})X_0R_5$, ethyl, vinyl, ethynyl, $C\equiv CC(O)OR_{86}$, $C\equiv CC(O)R_{87}$, acyl, formyl, cyano, carboxy, $C(O)OR_{89}$, $C(O)C(O)OR_{90}$,

$C(O)CH_2COOR_{91}$, $C(O)CH_2C(O)R_{88}$, cyanomethyl, $B(OH)_2$ or  , wherein

R_{16}, R_{17}, R_{18}, R_{20}, R_{21}, R_{22}, R_{23}, R_{24}, R_{25}, R_{26}, R_{27}, R_{28}, R_{38}, R_{39}, R_{40}, R_{41}, R_{42}, R_{43}, R_{50}, R_{53}, R_{56} and R_{57} are as defined in claim 1; R_5, R_9, R_{025}, R_{84}, R_{86}, R_{89}, R_{90} and R_{91} are each independently of the others C_1-C_4alkyl or phenyl; R_{10} and R_{85} are hydrogen or C_1-C_4alkyl; R_{87} and R_{88} are C_1-C_4alkyl, formyl, CH(C_1-C_4alkoxy) or C_1-C_4haloalkyl; X_2, X_3, X_4, X_6, X_7, X_8, X_9, X_{12}, X_{19}, X_{21} and Y_2 are oxygen or sulfur; and X_0 is oxygen, sulfur or amino, are new, and the present invention also relates to those compounds. Of those compounds, preference is given to those wherein A is fluorine, C_1-C_4alkylthio, C_1-C_4alkylsulfonyloxy, trifluoromethylsulfonyloxy, hydroxy, nitro, amino, isocyanato, isothiocyanato, hydrazino, a group $NHC(X_2)OR_5$, $NHC(X_7)OR_5$, $NHC(X_8)OR_5$, $NHC(X_9)OR_5$, $NHN=C(R_{17})C(O)R_{18}$, $NHC(X_7)N(R_{22})CR_{20}R_{21}C(O)OR_9$, $NHC(X_9)NR_{24}NR_{23}C(O)OR_{10}$, ethyl, vinyl, ethynyl, $C\equiv CC(O)OR_{86}$, $C\equiv CC(O)R_{87}$, acyl, formyl, cyano, carboxy, $C(O)OR_{89}$, $C(O)CH_2COOR_{91}$, $C(O)CH_2C(O)R_{88}$, cyanomethyl or $B(OH)_2$, wherein R_5, R_9, R_{10}, R_{86}, R_{89} and R_{91} are each independently of the others C_1-C_4alkyl; R_{17}, R_{18}, R_{20}, R_{21}, R_{22}, R_{23} and R_{24} are as defined for formula I; R_{87} and R_{88} are each independently of the other C_1-C_4alkyl, formyl, CH(C_1-C_4alkoxy) or C_1-C_4haloalkyl; and X_2, X_7, X_8 and X_9 are oxygen or sulfur.

The compounds of formula II wherein A is methyl, chlorine or bromine (compounds of formulae IIu and IIb) are known from CH-A-452 528, CH-A-452 529 and US-A-3 854 926 or can be prepared analogously to the processes described therein or analogously to Reaction Scheme 15.

The compounds of formula II wherein A is hydrogen (compounds of formula XXX) are known, for example, from Acta Chimica Scandinavica 23, 2322 (1969), CH-A-452 528, US-A-3 854 926 and WO 88/08705 or can be prepared analogously to the processes described therein or analogously to Reaction Scheme 15.

The compounds of formula XXVIII wherein, for example, A_0 is methyl or carboxy are known from CH-A-452 528 and J. Heterocyclic Chem. 13, 1103 (1976) or can be prepared analogously to the processes described therein.

The compounds of formula XXXI are either known, for example, where R_1 is hydrogen, from Acta Chimica Scandinavica, 23, 1785 (1969) and, where R_1 is chlorine or bromine, from Helv. Chim. Acta 60, 2062 (1977), or can be prepared analogously to the processes described therein.

Compounds of formulae XW and XIW are either known or can be prepared analogously to the processes described in WO 98/42698, WO 99/52892 and WO 99/52893.

The other compounds of formulae III, IV, V, VI, VIa, VIb, VIc, VI_0, VII, VIIa, VIIb, VIII, $VIII_0$, IX, IXa, IXb, X, Xa, XIa, XIb, XIc, XId, XIe, XIe_1, XIf, XIg, XIh, XIi, XIi_1, XIi_2, XIn, XII, XIII, $XIII_0$, XIV, XIVa, XIV_0, XVa, XVb, XVI, XVII, XVIII, XXV, XXVIa, XXVIb, XXVIc, XXVId, XXXII, XXXIII, XXXIVa, XXXIVb, XXXV, XXXVa, XXXVb, XXXVI, XXXVIIa, XXXVIIb, XXXVIII, XXXVIIIa, XXXVIIIb, XXXVIIIc, XXXVIIId, $XXXVIIId_1$, XXXIX, XL and XLI are known or can be prepared analogously to the processes described in the literature.

For the use according to the invention of the compounds of formula I or of compositions comprising them, there come into consideration all methods of application customary in agriculture, for example pre-emergence application, post-emergence application and seed dressing, and also various methods and techniques, such as, for example, the controlled release of active ingredient. For that purpose, a solution of the active ingredient is applied to mineral granule carriers or polymerised granules (urea-formaldehyde) and dried. If desired, it is also possible to apply a coating (coated granules) which allows the active ingredient to be released in metered amounts over a specific period of time.

The compounds of formula I can be used as herbicides in unmodified form, that is to say as they are obtained in synthesis, but they are preferably formulated in customary manner, together with the adjuvants conventionally employed in formulation technology, for example into emulsifiable concentrates, directly sprayable or dilutable solutions, dilute emulsions, wettable powders, soluble powders, dusts, granules or microcapsules. Such formulations are described, for example, in WO 97/34485 on pages 9 to 13. As with the nature of the compositions, the methods of application, such as spraying, atomising, dusting, wetting, scattering or pouring, are chosen in accordance with the intended objectives and the prevailing circumstances.

The formulations, that is to say the compositions, preparations or mixtures comprising the compound of formula I or at least one compound of formula I and, generally, one or more

solid or liquid formulation adjuvants, are prepared in known manner, for example by homogeneously mixing and/or grinding the active ingredients with the formulation adjuvants, for example solvents or solid carriers. Furthermore, surface-active compounds (surfactants) may also be used in the preparation of the formulations. Examples of solvents and solid carriers are given, for example, in WO 97/34485 on page 6.

Depending on the nature of the compound of formula I being formulated, suitable surface-active compounds are non-ionic, cationic and/or anionic surfactants and mixtures of surfactants having good emulsifying, dispersing and wetting properties.

Examples of suitable anionic, non-ionic and cationic surfactants are listed, for example, in WO 97/34485 on pages 7 and 8.

Furthermore, the surfactants customarily employed in formulation technology, which are described, *inter alia*, in "Mc Cutcheon's Detergents and Emulsifiers Annual" MC Publishing Corp., Ridgewood New Jersey, 1981, Stache, H., "Tensid-Taschenbuch", Carl Hanser Verlag, Munich/Vienna, 1981 and M. and J. Ash, "Encyclopedia of Surfactants", Vol I-III, Chemical Publishing Co., New York, 1980-81, are also suitable for preparation of the herbicidal compositions according to the invention.

The herbicidal formulations generally comprise from 0.1 to 99 % by weight, especially from 0.1 to 95 % by weight, of herbicide, from 1 to 99.9 % by weight, especially from 5 to 99.8 % by weight, of a solid or liquid formulation adjuvant and from 0 to 25 % by weight, especially from 0.1 to 25 % by weight, of a surfactant. Whereas commercial products will preferably be formulated as concentrates, the end user will normally employ dilute formulations. The compositions may also comprise further ingredients such as stabilisers, for example vegetable oils or epoxidised vegetable oils (epoxidised coconut oil, rapeseed oil or soybean oil), antifoams, for example silicone oil, preservatives, viscosity regulators, binders and tackifiers, as well as fertilisers or other active ingredients.

The compounds of formula I or a composition comprising that compound are generally applied to the plant or to the locus thereof at rates of application of from 0.001 to 4 kg/ha, especially from 0.005 to 2 kg/ha. The concentration required to achieve the desired effect can be determined by experiment. It is dependent on the nature of the action, the stage of development of the cultivated plant and of the weed and on the application (place, time, method) and may vary within wide limits as a function of those parameters.

The compounds of formula I are distinguished by herbicidal and growth-inhibiting properties, allowing them to be used in crops of useful plants, especially in cereals, cotton, soybeans, sugar beet, sugar cane, sorghum, plantation crops, rape, maize, sunflowers, vegetables, fodder plants and rice, and also for inhibiting plant growth and for non-selective weed control. Crops are to be understood as including also crops that have been made tolerant to herbicides or classes of herbicides as a result of conventional methods of breeding or genetic techniques. The weeds to be controlled may be either monocotyledonous or dicotyledonous weeds, for example Stellaria, Nasturtium, Agrostis, Digitaria, Avena, Setaria, Sinapis, Lolium, Solanum, Echinochloa, Scirpus, Monochoria, Sagittaria, Bromus, Alopecurus, Sorghum halepense, Rottboellia, Cyperus, Abutilon, Sida, Xanthium, Amaranthus, Brachiaria, Euphorbia, Chenopodium, Ipomoea, Chrysanthemum, Galium, Viola and Veronica.

The following Examples further illustrate but do not limit the invention.

Preparation Examples:

Example P1: 6-Nitro-4H-pyrido[3,2-b][1,4]oxazin-3-one

At 0-5°C, 150 g (1 mol) of 4H-pyrido[3,2-b][1,4]oxazin-3-one are introduced, in portions, into 400 ml of concentrated sulfuric acid. Then, while maintaining the temperature at below 10°C, 200 ml of fuming nitric acid are slowly added dropwise to the red solution and stirring is carried out for a further hour at 10-15°C. The reaction mixture is poured onto ice and the precipitated yellow product is filtered off and washed with cold water. Technical-grade 6-nitro-4H-pyrido[3,2-b][1,4]oxazin-3-one having a melting point of 247-252°C is thereby obtained which, after recrystallisation from methyl Cellosolve, melts at 254-256°C. ^{1}H-NMR ($(CD_3)_2SO$): 12.5 ppm (s, 1H); 8.00 ppm (d, J=8 Hz); 7.64 ppm (d, J=8.2 Hz); 4.88 ppm (s, 2H).

Example P2: 6-Amino-4H-pyrido[3,2-b][1,4]oxazin-3-one

156 g (0.8 mol) of the product obtained in Example P1 are dissolved in 2 litres of dimethyl-formamide and hydrogenated in the presence of 16 g of Raney nickel at 35-45°C until 53.8 litres of hydrogen have been absorbed. The mixture is then separated from the catalyst by filtration and diluted with water. Pure 6-amino-4H-pyrido[3,2-b][1,4]oxazin-3-one having a melting point of 279-281°C is thereby obtained. ^{1}H-NMR ($(CD_3)_2SO$): 10.78 ppm (s, NH); 7.03 ppm (d, 1H); 6.01 ppm (d, 1H); 6.29 ppm (s, 1H); 5.57 ppm (s, NH_2); 4.41 ppm (s, 2H).

Example P3: (3-Oxo-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazin-6-yl)-carbamic acid ethyl ester
1.45 g (8.8 mmol) of 6-amino-4H-pyrido[3,2-b][1,4]oxazin-3-one are dissolved in 60 ml of pyridine and treated with 0.96 g (8.8 mmol) of chloroformic acid ethyl ester at 45°C. Stirring is then carried out for about 3 hours at that temperature, the precipitated pyridine hydrochloride is filtered off and the mixture is concentrated a little by evaporation. 150 ml of water are then added to the mixture, the pH is adjusted to 4 using concentrated hydrochloric acid and the precipitated crystals are filtered off. Virtually pure (3-oxo-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazin-6-yl)-carbamic acid ethyl ester is thereby obtained.
^{1}H-NMR ($(CD_3)_2SO$): 11.08 ppm (s, NH); 9.78 ppm (s, NH); 7.33 ppm (m, 2H); 4.57 ppm (s, 2H); 4.12 ppm (q, 2H); 1.22 ppm (t, 3H).

Example P4: 3-(3-Oxo-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazin-6-yl)-6-trifluoromethyl-1H-pyrimidine-2,4-dione
1.5 g (6.3 mmol) of (3-oxo-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazin-6-yl)-carbamic acid ethyl ester are introduced into a suspension of 0.36 g (15 mmol) of sodium hydride in N-methyl-pyrrolidone. Stirring is then carried out for about 30 minutes at 35°C, 1.3 g (7.3 mmol) of 3-amino-4,4,4-trifluoro-but-2-enoic acid ethyl ester are then added thereto, and the reaction mixture is heated at 100°C for 1.5 hours. Ice-water is added, the pH is adjusted to 2 using hydrochloric acid and the mixture is extracted several times with ethyl acetate. The combined organic phases are concentrated by evaporation to a volume of about 50 ml, whereupon 3-(3-oxo-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazin-6-yl)-6-trifluoromethyl-1H-pyrimidine-2,4-dione precipitates out as an almost pure product.
^{1}H-NMR ($(CD_3)_2SO$): 12.65 ppm (broad signal, NH); 11.40 ppm (s, NH); 7.52 ppm (d, 1H); 7.05 ppm (d, 1H); 6.36 ppm (s, 1H); 4.72 ppm (s, 2H).

Example P5: 1-Methyl-3-(4-methyl-3-oxo-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazin-6-yl)-6-trifluoromethyl-1H-pyrimidine-2,4-dione
0.33 g (1.0 mmol) of 3-(3-oxo-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazin-6-yl)-6-trifluoromethyl-1H-pyrimidine-2,4-dione is stirred with 0.31 g (2.0 mmol) of methyl iodide in the presence of 0.27 g (2.0 mmol) of potassium carbonate in 5 ml of acetonitrile at 20°C. After then being stirred for about 16 hours at 40-45°C, 30 ml of water are added and the mixture is acidified to pH 5 using hydrochloric acid and extracted with ethyl acetate. The product is purified by column chromatography (mobile phase: ethyl acetate/hexane 1/1). Pure 1-methyl-3-(4-methyl-3-oxo-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazin-6-yl)-6-trifluoromethyl-1H-pyrimidine-2,4-dione having a melting point of 211-211.5°C is obtained.

^{1}H-NMR ($CDCl_3$): 7.38 ppm (d, 1H); 6.90 ppm (d, 1H); 6.39 ppm (s, 1H); 4.74 ppm (s, 2H); 3.57 ppm (s, 3H); 3.41 ppm (s, 3H).

Example P6: 1-Methyl-3-(3-oxo-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazin-6-yl)-6-trifluoromethyl-1H-pyrimidine-2,4-dione

0.78 g (2.4 mmol) of 3-(3-oxo-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazin-6-yl)-6-trifluoromethyl-1H-pyrimidine-2,4-dione is stirred with 0.37 g (2.4 mmol) of methyl iodide in the presence of 0.25 g of potassium hydrogen carbonate in 5 ml of dimethylformamide at 20°C. After about 6 hours, 30 ml of water are added and the precipitated product is filtered off. Virtually pure 1-methyl-3-(3-oxo-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazin-6-yl)-6-trifluoromethyl-1H-pyrimidine-2,4-dione is obtained.

^{1}H-NMR ($(CD_3)_2SO$): 11.32 ppm (s, NH); 7.53 ppm (d, 1H); 7.01 ppm (d, 1H); 6.53 ppm (s, 1H); 4.74 ppm (s, 2H); 3.32 ppm (s, 3H).

Example P7: 1-Methyl-3-(3-oxo-4-prop-2-ynyl-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazin-6-yl)-6-trifluoromethyl-1H-pyrimidine-2,4-dione

0.30 g (0.9 mmol) of 1-methyl-3-(3-oxo-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazin-6-yl)-6-trifluoromethyl-1H-pyrimidine-2,4-dione and 0.11 g (0.9 mmol) of propargyl bromide are heated in the presence of 0.14 g of potassium carbonate and a catalytic amount of 18-crown-6 in 10 ml of acetonitrile for 1 hour at reflux temperature. The solvent is evaporated off and the residue is filtered using a 1:1 mixture of ethyl acetate/hexane over a small amount of silica gel. The desired 1-methyl-3-(3-oxo-4-prop-2-ynyl-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazin-6-yl)-6-trifluoromethyl-1H-pyrimidine-2,4-dione is obtained in the pure form having a melting point of 161.5-162°C.

Example P8: 3-(4-Isopropyl-3-oxo-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazin-6-yl)-1-methyl-6-trifluoromethyl-1H-pyrimidine-2,4-dione

0.30 g (0.9 mmol) of 1-methyl-3-(3-oxo-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazin-6-yl)-6-trifluoromethyl-1H-pyrimidine-2,4-dione and 0.17 g (1.4 mmol) of isopropyl bromide are heated at 120°C in the presence of 0.19 g (1.4 mmol) of potassium carbonate and a catalytic amount of 18-crown-6 and a catalytic amount of potassium iodide in 2 ml of dimethylformamide in a pressure vessel for about 2 hours. The solvent is evaporated off under reduced pressure and the residue is chromatographed using a 1:2 mixture of ethyl acetate and hexane on silica gel. Pure 3-(4-isopropyl-3-oxo-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazin-6-yl)-1-methyl-6-trifluoromethyl-1H-pyrimidine-2,4-dione is thereby obtained.

^{1}H-NMR ($CDCl_3$): 7.36 ppm (d, 1H); 6.87 ppm (d, 1H); 6.37 ppm (s, 1H); 5.16 ppm (m, 1H); 4.64 ppm (s, 2H); 3.57 ppm (s, 3H); 1.50 ppm (d, 6H).

Example P9: 6-(4-Chloro-5-difluoromethoxy-1-methyl-1H-pyrazol-3-yl)-7-fluoro-4H-pyrido[3,2-b][1,4]oxazin-3-one

0.5 g (1.3 mmol) of 2-(3-chloro-6-(4-chloro-5-difluoromethoxy-1-methyl-1H-pyrazol-3-yl)-5-fluoro-pyridin-2-yloxy)acetamide (WO 98/42698) is heated at 150°C in the presence of 0.18 g (1.3 mmol) of potassium carbonate in 10 ml of N-methylpyrrolidone (NMP) for 2 hours. The mixture is poured into water and extracted with diethyl ether. The residue that remains is chromatographed on silica gel. Pure 6-(4-chloro-5-difluoromethoxy-1-methyl-1H-pyrazol-3-yl)-7-fluoro-4H-pyrido[3,2-b][1,4]oxazin-3-one is thereby obtained as the more polar fraction.

^{1}H-NMR ($CDCl_3$): 8.40 ppm (s, NH); 7.18 ppm (d, 1H); 6.71 ppm (t, 1H); 4.74 ppm (s, 2H); 3.85 ppm (s, 3H).

Example P10: 3-Oxo-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazine-6-carboxylic acid

3.66 g (84 mmol) of sodium hydride in the form of a 55 % dispersion in oil are introduced into 30 ml of dimethylformamide; then, 6.2 g of (40 mmol) of 2-amino-3-hydroxypyridin-6-yl-carboxylic acid (known from J. Heterocycl. Chem. 13, 1103 (1976)) are introduced, in portions, below 10°C and stirring is then carried out for 2 hours at 45°C until the evolution of hydrogen has ceased. 5.4 ml (44 mmol) of bromoacetic acid ethyl ester are then added dropwise. The suspension, which is difficult to stir, is further diluted with 15 ml of dimethylformamide and stirring is carried out for a further 2 hours at 70°C. The mixture is left to warm up to 20°C, water is added and extraction at pH 8 is carried out with diethyl ether. The aqueous phase is adjusted to pH 2.6 using hydrochloric acid and extracted with ethyl acetate. The residue is taken up in diethyl ether and readily soluble components are removed by filtration. Pure 3-oxo-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazine-6-carboxylic acid having a melting point of 138-140°C is obtained as a crystalline product.

^{1}H-NMR ($(CD_3)_2SO$): 12.98 ppm (broad signal, OH); 11.55 ppm (s, NH); 7.66 ppm (d, 1H); 7.41 ppm (d, 1H); 4.72 ppm (s, 2H).

Example P11: 3-(2-Methyl-3-oxo-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazin-6-yl)-3-oxo-propionic acid ethyl ester

1.3 g (7.3 mmol) of the potassium salt of malonic acid monomethyl ester and 0.88 g (9.2 mmol) of magnesium chloride are introduced into 20 ml of acetonitrile at 10°C, 1.5 ml (1.1 mmol) of triethylamine are added and stirring is carried out at 20°C for 1 hour. There is

then added 0.96 g (3.7 mmol) of crude 2-methyl-3-oxo-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazine-6-carboxylic acid chloride (^{1}H-NMR ($CDCl_3$): 8.38 ppm (broad signal, NH); 7.88 ppm (d, 1H); 7.38 ppm (d, 1H); 4.36 ppm (q, 1H); 1.63 ppm (d, 3H)), prepared from 0.82 g (4 mmol) of 2-methyl-3-oxo-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazine-6-carboxylic acid (Example II.026) by heating with 0.45 ml (5 mmol) of oxalyl chloride in 15 ml of hexane and a catalytic amount of dimethylformamide, and stirring is carried out for a further 3 hours. The reaction mixture is then poured into ice-water and adjusted to pH 3 using 32 % hydrochloric acid. Extraction with ethyl acetate is carried out; washing once with 5 % sodium hydrogen carbonate solution and once with saturated sodium chloride solution and concentration by evaporation are carried out. The tautomeric forms of the desired title compound 3-hydroxy-3-(2-methyl-3-oxo-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazin-6-yl)-acrylic acid ethyl ester are thereby obtained in the form of an oil. ^{1}H-NMR ($CDCl_3$): 8.02 ppm (broad signal, OH); 7.78 ppm (d, 1H); 7.32 ppm (d, 1H); 7.70 ppm (q, 1H); 4.18 ppm (q, 2H); 4.04 ppm (s, 1H); 1.62 ppm (d, 3H); 1.24 ppm (t, 3H).

Example P12: 6-(5-Hydroxy-1-methyl-1H-pyrazol-3-yl)-2-methyl-4H-pyrido[3,2-b][1,4]oxazin-3-one

0.82 g (2.9 mmol) of the product prepared in Example P11 is dissolved in 5 ml of acetic acid, and 0.19 ml (3.5 mmol) of methylhydrazine is added. Heating at 80°C is carried out for 4 hours and the mixture is then concentrated by evaporation. The desired 6-(5-hydroxy-1-methyl-1H-pyrazol-3-yl)-2-methyl-4H-pyrido[3,2-b][1,4]oxazin-3-one is obtained in the form of crystals by means of column chromatography (mobile phase: ethyl acetate/hexane 1/1). ^{1}H-NMR ($(CD_3)_2SO$): 11.35 ppm (s, NH); 7.58 ppm (d, 1H); 7.49 ppm (d, 1H); 5.98 ppm (s, 1H); 4.92 ppm (q, 1H); 3.71 ppm (s, 3H); 1.61 ppm (d, 3H).

Example P13: 6-(5-Difluoromethoxy-1-methyl-1H-pyrazol-3-yl)-2-methyl-4H-pyrido[3,2-b]-[1,4]oxazin-3-one

0.36 g (1.4 mmol) of the product prepared in Example P12 is stirred in the presence of 0.55 g (13.8 mmol) of sodium hydroxide in a mixture of 8 ml of dioxane and 8 ml of water at 70°C for 1 hour while continuously passing gaseous Freon (bromo-difluoromethane) into the mixture. The temperature is maintained at 80°C for a further 30 minutes and the mixture is then adjusted to pH 4 using hydrochloric acid and extracted with ethyl acetate. The desired 6-(5-difluoromethoxy-1-methyl-1H-pyrazol-3-yl)-2-methyl-4H-pyrido[3,2-b][1,4]oxazin-3-one is thereby obtained.

^{1}H-NMR ($(CD_3)_2SO$): 11.60 ppm (s, NH); 7.38 ppm (d, 1H); 7.32 ppm (d, 1H); 7.26 ppm (t, 1H); 5.78 ppm (s, 1H); 4.68 ppm (q, 1H); 3.65 ppm (s, 3H); 1.34 ppm (d, 3H).

Example P14: 6-(4-Chloro-5-difluoromethoxy-1-methyl-1H-pyrazol-3-yl)-2-methyl-4H-pyrido-[3,2-b][1,4]oxazin-3-one

In the presence of 0.09 g (0.11 mmol) of sodium acetate in 4 ml of acetic acid, 0.07 g (0.22 mmol) of the product prepared in Example P13 is treated, dropwise, at 60°C, with a solution of 0.015 g (0.22 mmol) of chlorine gas in acetic acid. After the reaction has terminated, the mixture is concentrated by evaporation and purified by chromatography on silica gel. The desired 6-(4-chloro-5-difluoromethoxy-1-methyl-1H-pyrazol-3-yl)-2-methyl-4H-pyrido[3,2-b][1,4]oxazin-3-one is thereby obtained.

^{1}H-NMR ($CDCl_3$): 8.45 ppm (s, NH); 7.68 ppm (d, 1H); 7.52 ppm (d, 1H); 6.68 ppm (t, 1H); 4.74 ppm (q, 1H); 3.85 ppm (s, 3H); 1.64 ppm (d, 3H).

Example P15: 2-(3-Oxo-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazin-6-yl)-4,5,6,7-tetrahydro-isoindole-1,3-dione

1.65 g (10 mmol) of 6-amino-4H-pyrido[3,2-b][1,4]oxazin-3-one (Example P2) and 1.67 g (10 mmol) of tetrahydrophthalic acid anhydride are heated at boiling point in 10 ml of acetic acid for 7 hours. The mixture is then concentrated by evaporation and stirred in hot ethyl acetate. Pure 2-(3-oxo-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazin-6-yl)-4,5,6,7-tetrahydro-isoindole-1,3-dione is obtained as an insoluble residue having a melting point of 220°C. ^{1}H-NMR ($CDCl_3$): 8.72 ppm (broad signal, NH); 7.38 ppm (d, 1H); 6.94 ppm (d, 1H); 4.68 ppm (s, 2H); 2.42 ppm (m, 2H); 1.80 ppm (m, 2H).

Example P16: 6-Amino-4-prop-2-ynyl-4H-pyrido[3,2-b][1,4]oxazin-3-one

4.95 g (30 mmol) of 6-amino-4H-pyrido[3,2-b][1,4]oxazin-3-one (Example P2) and 3.75 g (31 mmol) of propargyl bromide are heated at boiling point in 30 ml of acetonitrile in the presence of 4.15 g (30 mmol) of potassium carbonate and a catalytic amount of 18-crown-6 for 5 hours. The product is then extracted with ethyl acetate from an aqueous solution at pH 8 and the residue, after concentration by evaporation, is purified by chromatography. Pure 6-amino-4-prop-2-ynyl-4H-pyrido[3,2-b][1,4]oxazin-3-one having a melting point of 125.5-126°C is obtained.

Example P17: 6-Isocyanato-4-prop-2-ynyl-4H-pyrido[3,2-b][1,4]oxazin-3-one

3.5 g (17.2 mmol) of the above product from Example P16 are dissolved in 40 ml of ethyl acetate and treated with 1.87 g (9.5 mmol) of diphosgene. After the slightly exothermic reaction has subsided, the mixture is heated at 60°C for 2 hours, a clear solution being obtained. The reaction mixture is concentrated by evaporation and the crude 6-isocyanato-

4-prop-2-ynyl-4H-pyrido[3,2-b][1,4]oxazin-3-one in the form of amorphous crystals is used directly for subsequent reactions (e.g. in Example P18). For the purpose of identification, a sample of the reaction mixture is stirred in methanol in the presence of a small amount of triethylamine. According to a thin-layer chromatogram, the precipitated product is (3-oxo-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazin-6-yl)-carbamic acid methyl ester.

Example P18: 7-<R,S>-Hydroxy-2-(3-oxo-4-prop-2-ynyl-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazin-6-yl)-tetrahydro-imidazo[1,5-a]pyridine-1,3-dione

0.46 g (2.3 mmol) of 4-hydroxy-piperidine-2-carboxylic acid methyl ester • hydrochloride is introduced into 15 ml of dichloromethane at 20°C. 0.50 g (5 mmol) of triethylamine is added and stirring is then carried out for 5 minutes. A dichloromethane solution of 0.54 g (2.3 mmol) of the 6-isocyanato-4-prop-2-ynyl-4H-pyrido[3,2-b][1,4]oxazin-3-one prepared above in Example P17 is then introduced dropwise and stirring is carried out at about 35°C for a further 3 hours. The reaction mixture is then concentrated by evaporation and, in order to remove insoluble components, it is filtered directly with ethyl acetate over a silica gel column. Pure 7-<R,S>-hydroxy-2-(3-oxo-4-prop-2-ynyl-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazin-6-yl)-tetrahydro-imidazo[1,5-a]pyridine-1,3-dione is obtained as an isomeric mixture having a melting point of 205.5-206°C.

Example P19: 7-<R> and 7-<S>-Fluoro-2-(3-oxo-4-prop-2-ynyl-3,4-dihydro-2H-pyrido[3,2-b]-[1,4]oxazin-6-yl)-tetrahydro-imidazo[1,5-a]pyridine-1,3-dione

0.16 g (0.45 mmol) of racemic 7-hydroxy-2-(3-oxo-4-prop-2-ynyl-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazin-6-yl)-tetrahydro-imidazo[1,5-a]pyridine-1,3-dione (Example P18) is treated in 5 ml of pyridine at -10°C with a solution of 0.11 g (0.68 mmol) of diethylaminosulfur trifluoride (DAST) in 1 ml of dichloromethane. The mixture is left to warm up to 20°C slowly and is stirred overnight. The mixture is then concentrated by evaporation and the aqueous solution at pH 6 is extracted with ethyl acetate, dried and concentrated by evaporation again. The first isomer, 7-<R> or 7-<S>-fluoro-2-(3-oxo-4-prop-2-ynyl-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazin-6-yl)-tetrahydro-imidazo[1,5-a]pyridine-1,3-dione, is obtained by column chromatography (mobile phase: ethyl acetate/hexane 1/1). ^{1}H-NMR ($CDCl_3$): 7.38 ppm (d, 1H); 7.04 ppm (d, 1H); 5.90 ppm (m, 1H); 4.86 ppm (m, 2H); 4.72 ppm (s, 2H). Further elution then yields the second isomer, 7-<R> or 7-<S>-fluoro-2-(3-oxo-4-prop-2-ynyl-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazin-6-yl)-tetrahydro-imidazo[1,5-a]pyridine-1,3-dione. ^{1}H-NMR ($CDCl_3$): 7.36 ppm (d, 1H); 7.01 ppm (d, 1H); 5.20 ppm (m, 1H); 4.86 ppm (m, 2H); 4.73 ppm (s, 2H).

Example P20: 1-Amino-3-(3-oxo-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazin-6-yl)-6-trifluoromethyl-1H-pyrimidine-2,4-dione

3.28 g (10 mmol) of 3-(3-oxo-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazin-6-yl)-6-trifluoromethyl-1H-pyrimidine-2,4-dione (Example P4) are stirred with 2.59 g (13 mmol) of N-2,4-dinitrophenyl-hydroxylamine in the presence of 1.22 g (14.5 mmol) of sodium hydrogen carbonate in 50 ml of dimethylformamide at 20°C for 35 hours. Water is added and extraction with ethyl acetate is carried out; the organic phase is washed twice with small amounts of water, dried over magnesium sulfate and concentrated, in part, by evaporation. The desired title compound, 1-amino-3-(3-oxo-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazin-6-yl)-6-trifluoromethyl-1H-pyrimidine-2,4-dione having a melting point of >220°C precipitates in the form of crystals from the ethyl acetate phase. ^{1}H-NMR ($(CD_3)_2SO$): 11.32 ppm (s, NH); 7.46 ppm (d, 1H); 6.95 ppm (d, 1H); 6.29 ppm (s, 1H); 5.48 ppm (s, NH_2); 4.68 ppm (s, 2H).

Example P21: 6-Isothiocyanato-4H-pyrido[3,2-b][1,4]oxazin-3-one

16.5 g (0.1 mol) of 6-amino-4H-pyrido[3,2-b][1,4]oxazin-3-one (Example P2) are introduced into 200 ml of ethyl methyl ketone and, over a period of 20 minutes, 13.8 g (0.12 mol) of thiophosgene are added. Stirring is then carried out at 22-28°C for 90 minutes and then 10 g (0.12 mol) of solid sodium hydrogen carbonate are first added to the mixture and then 100 ml of water are added dropwise. After the evolution of gas has ceased, stirring is continued for a further 90 minutes and extraction with 1000 ml of ethyl acetate is carried out. The aqueous phase, which contains solid components, is extracted a further three times, using 200 ml of ethyl acetate each time. The combined organic extracts are dried, filtered over Hyflo™ and concentrated until crystallisation occurs. The title compound is obtained in pure form as an ochre-coloured powder having a melting point of 178-179°C. ^{1}H-NMR ($(CD_3)_2SO$): 11.42 ppm (s, NH); 7.34 ppm (d, 1H); 6.88 ppm (d, 1H); 4.62 ppm (s, 2H).

Example P22: 6-(6-Oxo-2-thioxo-4-trifluoromethyl-3,6-dihydro-2H-pyrimidin-1-yl)-4H-pyrido-[3,2-b][1,4]oxazin-3-one

3.3 g (18 mmol) of 3-amino-4,4,4-trifluoro-but-2-enoic acid ethyl ester are added dropwise at 0°C to 1.6 g (37 mmol) of sodium hydride in 15 ml of N-methylpyrrolidone as a 55 % dispersion in oil. After stirring for 15 minutes and after the evolution of hydrogen has ceased, 3.1 g (15 mmol) of 6-isothiocyanato-4H-pyrido[3,2-b][1,4]oxazin-3-one (Example P21) are added to the mixture, which is heated gradually to 90°C. After a further hour, the

mixture is cooled, water is added, the pH is adjusted to 9 and the mixture is washed twice with ethyl acetate. The aqueous phase is then acidified to pH 2 using concentrated hydrochloric acid, whereupon the product precipitates out in the form of crystals, which are filtered off and yield pure 6-(6-oxo-2-thioxo-4-trifluoromethyl-3,6-dihydro-2H-pyrimidin-1-yl)-4H-pyrido[3,2-b][1,4]oxazin-3-one having a melting point of >220°C. ^{1}H-NMR ($(CD_3)_2SO$): 11.39 ppm (s, NH); 7.49 ppm (d, 1H); 7.01 ppm (d, 1H); 6.68 ppm (s, 1H); 4.72 ppm (s, 2H).

Example P23: Tetrahydro-pyridazine-1-carbothionic acid (3-oxo-3,4-dihydro-2H-pyrido-[3,2-b][1,4]oxazin-6-yl)-amide

9.15 g (55 mmol) of tetrahydropyridazine dihydrochloride are introduced into 150 ml of ethanol. There are then added, in succession, 11.6 g (115 mmol) of triethylamine and then, in portions, 10.4 g (50 ml) of the compound prepared in Example P21, 6-isothiocyanato-4H-pyrido[3,2-b][1,4]oxazin-3-one, the temperature being maintained between 23° and 28°C. After stirring for one hour, the precipitated product is filtered off, washed thoroughly with water and ethanol/water 1/1 and then dried *in vacuo* at 70°C. Pure tetrahydro-pyridazine-1-carbothionic acid (3-oxo-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazin-6-yl)-amide having a melting point of 212-212.5°C is obtained.

Example P24: 6-[3-Oxo-tetrahydro-[1,3,4]thiadiazolo[3,4-a]pyridazin-<1E>- and -<1Z>-ylideneamino]-4H-pyrido[3,2-b][1,4]oxazin-3-one and 6-(1-oxo-3-thioxo-tetrahydro-[1,2,4]triazolo[1,2-a]pyridazin-2-yl)-4H-pyrido[3,2-b][1,4]oxazin-3-one

1.47 g (5 mmol) of tetrahydro-pyridazine-1-carbothionic acid (3-oxo-3,4-dihydro-2H-pyrido-[3,2-b][1,4]oxazin-6-yl)-amide (Example P23) and 1.83 g (18 mmol) of triethylamine are introduced into 80 ml of tetrahydrofuran, whereupon a clear solution is obtained. At 5-10°C, 3.1 ml of a 20 % solution of 0.58 g (5.9 mmol) of phosgene in toluene are added slowly thereto and stirring is carried out overnight at 20°C. The solvents are distilled off under reduced pressure and the dry residue is triturated in 100 ml of water. The crystals that precipitate out are filtered off, taken up while hot in 80 ml of fresh tetrahydrofuran and poorly soluble components are removed by filtering again. Pure 6-[3-oxo-tetrahydro-[1,3,4]thiadiazolo[3,4-a]pyridazin-<1E>- or -<1Z>-ylideneamino]-4H-pyrido[3,2-b][1,4]oxazin-3-one (= product A, Example 12.001) having a melting point of >225°C is thereby obtained. ^{1}H-NMR ($(CD_3)_2SO$): 11.40 ppm (s, NH); 7.51 ppm (d, 1H); 6.81 ppm (d, 1H); 4.78 ppm (s, 2H); 3.97 ppm (m, 2H); 3.75 ppm (m, 2H); 1.90 ppm (m, 4H).

The mother liquor is concentrated by evaporation and yields, after filtration over silica gel (mobile phase hexane/tetrahydrofuran 3/2), approx. 80 % 6-(1-oxo-3-thioxo-tetrahydro-[1,2,4]triazolo[1,2-a]pyridazin-2-yl)-4H-pyrido[3,2-b][1,4]oxazin-3-one having a melting point

of >225°C (= product B), which is contaminated with approx. 20 % product A. ^{1}H-NMR ($(CD_3)_2SO$): 11.50 ppm (s, NH); 7.68 ppm (d, 1H); 7.21 ppm (d, 1H); 4.91 ppm (s, 2H); 4.56 ppm (m, 2H); 3.68 ppm (m, 2H); 2.02 ppm (m, 4H).

Example P25: 6-[3-Oxo-tetrahydro-[1,3,4]thiadiazolo[3,4-a]pyridazin-<1E>- and/or -<1Z>-ylideneamino]-4-prop-2-ynyl-4H-pyrido[3,2-b][1,4]oxazin-3-one and 6-(1-oxo-3-thioxo-tetrahydro-[1,2,4]triazolo[1,2-a]pyridazin-2-yl)-4-prop-2-ynyl-4H-pyrido[3,2-b][1,4]oxazin-3-one

0.35 g (1.1 mmol) of the 4/1 mixture of product B isolated in Example P24 is heated at boiling point in the presence of 0.15 g (1.3 mmol) of propargyl bromide, 0.18 g (1.3 mmol) of potassium carbonate and a catalytic amount of 18-crown-6 in 10 ml of acetonitrile and 3 ml of N-methylpyrrolidone for 2.5 hours. The mixture is then concentrated by evaporation and the residue is chromatographed on silica gel (mobile phase ethyl acetate/hexane 1/1); pure 6-[3-oxo-tetrahydro-[1,3,4]thiadiazolo[3,4-a]pyridazin-<1E>- and/or -<1Z>-ylideneamino]-4-prop-2-ynyl-4H-pyrido[3,2-b][1,4]oxazin-3-one is first isolated as product A having a melting point of >225°C. ^{1}H-NMR ($(CD_3)_2SO$): 7.28 ppm (d, 1H); 6.78 ppm (d, 1H); 4.92 ppm (d, 2H); 4.68 ppm (s, 2H); 3.90 ppm (m, 2H); 3.74 ppm (m, 2H); 2.20 ppm (t, 2H); 1.90 ppm (m, 4H). Pure 6-(1-oxo-3-thioxo-tetrahydro-[1,2,4]triazolo[1,2-a]pyridazin-2-yl)-4-prop-2-ynyl-4H-pyrido[3,2-b][1,4]oxazin-3-one having a melting point of >225°C is isolated thereafter as main product B. ^{1}H-NMR ($(CD_3)_2SO$): 7.41 ppm (d, 1H); 7.13 ppm (d, 1H); 4.88 ppm (d, 2H); 4.77 ppm (s, 2H); 4.04 ppm (m, 2H); 3.74 ppm (m, 2H); 2.17 ppm (t, 2H); 1.98 ppm (m, 4H).

Example P26: (3-Oxo-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazin-6-yl)-thiocarbamic acid O-ethyl ester

15.5 g (75 mmol) of 6-isothiocyanato-4H-pyrido[3,2-b][1,4]oxazin-3-one (Example P21) are heated in 300 ml of absolute ethanol at boiling point for 1 hour. From the reaction mixture, which has been cooled to 10°C, there can be obtained pure (3-oxo-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazin-6-yl)-thiocarbamic acid O-ethyl ester having a melting point of 218.5-219°C.

Example P27: 6-(4,5-Dihydro-1H-imidazol-2-ylamino)-4H-pyrido[3,2-b][1,4]oxazin-3-one

5.7 g (20 mmol) of (3-oxo-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazin-6-yl)-thiocarbamic acid O-ethyl ester (Example P26) are heated in 20 ml of ethylenediamine at 80°C for 90 minutes. The solid product that precipitates out is pure 6-(4,5-dihydro-1H-imidazol-2-ylamino)-4H-pyrido[3,2-b][1,4]oxazin-3-one having a melting point of >225°C.

Example P28: 6-(7-Oxo-5-trifluoromethyl-2,3-dihydro-7H-imidazo[1,2-a]pyrimidin-8-yl)-4H-pyrido[3,2-b][1,4]oxazin-3-one

3.3 g (14.1 mmol) of 6-(4,5-dihydro-1H-imidazol-2-ylamino)-4H-pyrido[3,2-b][1,4]oxazin-3-one (Example P27) and 3.2 g (16.3 mmol) of 3-amino-4,4,4-trifluoro-but-2-enoic acid ethyl ester are heated in 12 ml of N-methylpyrrolidone at 135°C for 8 hours. Water is added thereto and extraction is carried out several times with warm ethyl acetate. From the combined organic phases there crystallises, on concentration by evaporation, pure 6-(7-oxo-5-trifluoromethyl-2,3-dihydro-7H-imidazo[1,2-a]pyrimidin-8-yl)-4H-pyrido[3,2-b][1,4]oxazin-3-one having a melting point of >225°C. ^{1}H-NMR ($(CD_3)_2SO$): 11.46 ppm (s, NH); 7.56 ppm (d, 1H); 7.06 ppm (d, 1H); 6.02 ppm, (s, 1H), 4.69 ppm (s, 2H), 4.22 ppm (t, 2H); 3.80 ppm (t, 3H).

Example P29: 6-(2-Methyl-7-oxo-5-trifluoromethyl-2,3-dihydro-7H-imidazo[1,2-a]pyrimidin-8-yl)-4-(1-methyl-prop-2-ynyl)-4H-pyrido[3,2-b][1,4]oxazin-3-one

0.31 g (0.85 mmol) of 6-(2-methyl-7-oxo-5-trifluoromethyl-2,3-dihydro-7H-imidazo[1,2-a]-pyrimidin-8-yl)-4H-pyrido[3,2-b][1,4]oxazin-3-one (Example 11.002) and 0.28 g (0.19 mmol) of 3-mesyloxy-but-1-yne are heated in the presence of approx. 0.23 g (1.9 mmol) of potassium carbonate and a catalytic amount of 18-crown-6 in 10 ml of tetrahydrofuran and 5 ml of N-methylpyrrolidone in a small pressure reactor at an internal temperature of 110°C for 4 hours. The reaction mixture is then extracted from an aqueous phase by shaking with ethyl acetate and is separated by chromatography over silica gel using ethyl acetate/methanol 9/1 as mobile phase into the two racemic <S,S> or <R,R> and <S,R> or <R,S> isomers of 6-(2-methyl-7-oxo-5-trifluoromethyl-2,3-dihydro-7H-imidazo[1,2-a]pyrimidin-8-yl)-4-(1-methyl-prop-2-ynyl)-4H-pyrido[3,2-b][1,4]oxazin-3-one. Isomer I: ^{1}H-NMR ($CDCl_3$): 7.32 ppm (d, 1H); 7.02 ppm (d, 1H); 6.04 ppm (qxd, 1H); 5.84 ppm (s, 1H); 5.88 ppm (s, 1H); 4.68 ppm (s, 2H), 4.2 ppm (m, 2H); 3.58 ppm (m, 1H); 2.52 ppm (m, 1H); 1.61 ppm (d, 3H); 1.30 ppm (m, 3H). Isomer II: ^{1}H-NMR ($CDCl_3$): 7.40 ppm (d, 1H); 6.98 ppm (d, 1H); 5.94 ppm (qxd, 1H); 5.88 ppm (s, 1H); 4.69 ppm (s, 2H), 4.2 ppm (m, 2H); 3.65 ppm (m, 1H); 2.30 ppm (m, 1H); 1.72 ppm (dxd, 3H); 1.30 ppm (m, 3H).

Example P30: 3-(4-n-Propyl-3-oxo-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazin-6-yl)-5-chloro-1-methyl-6-trifluoromethyl-1H-pyrimidine-2,4-dione

0.17 g (0.44 mmol) of 3-(4-n-propyl-3-oxo-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazin-6-yl)-1-methyl-6-trifluoromethyl-1H-pyrimidine-2,4-dione (Example 1.060) is treated, in the presence of 0.15 g (1.7 mmol) of sodium acetate in 5 ml of acetic acid at 40°C, with chlorine gas until all the starting material has completely reacted. Extraction with ethyl acetate is

then carried out; washing once with sodium acetate solution, drying and recrystallisation are carried out. Pure 3-(4-n-propyl-3-oxo-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazin-6-yl)-5-chloro-1-methyl-6-trifluoromethyl-1H-pyrimidine-2,4-dione having a melting point of 176-178°C is thereby obtained. ^{1}H-NMR ($CDCl_3$): 7.38 ppm (d, 1H); 6.87 ppm (d, 1H); 4.72 ppm (s, 2H), 4.01 ppm (m, 2H); 3.62 ppm (s, 3H); 1.67 ppm (m, 2H); 0.90 ppm (t, 3H).

Example P31: 6-(2-Fluoromethoxy-6-oxo-4-trifluoromethyl-6H-pyrimidin-1-yl)-4-prop-2-ynyl-4H-pyrido[3,2-b][1,4]oxazin-3-one and 1-fluoromethyl-3-(3-oxo-4-prop-2-ynyl-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazin-6-yl)-6-trifluoromethyl-1H-pyrimidine-2,4-dione

0.19 g (0.52 mmol) of 3-(3-oxo-4-prop-2-ynyl-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazin-6-yl)-6-trifluoromethyl-1H-pyrimidine-2,4-dione (Example 1.006) is introduced into 5 ml of dimethylformamide in the presence of 0.09 g (0.67 mmol) of potassium carbonate and, at 0°C, is treated with 0.25 ml of bromofluoromethane. The mixture is left to warm up to 20°C overnight, with vigorous stirring; the reaction mixture is then taken up in diethyl ether and the diethyl ether phase is washed once with dilute hydrochloric acid and once with sodium chloride solution. The residue is concentrated by evaporation and then separated by HPLC (mobile phase gradient from 30 to 40 % ethyl acetate in hexane) into two products, there being obtained, as less polar component, 6-(2-fluoromethoxy-6-oxo-4-trifluoromethyl-6H-pyrimidin-1-yl)-4-prop-2-ynyl-4H-pyrido[3,2-b][1,4]oxazin-3-one having ^{1}H-NMR ($CDCl_3$): 7.46 ppm (d, 1H); 6.98 ppm (d, 1H); 6.72 ppm (s, 1H); 5.95 ppm (d, J=50Hz, 1H); 4.82 ppm (4H); 2.12 ppm (t, 1H), and, as more polar component, 1-fluoromethyl-3-(3-oxo-4-prop-2-ynyl-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazin-6-yl)-6-trifluoromethyl-1H-pyrimidine-2,4-dione having a melting point of 192-193°C and ^{1}H-NMR ($CDCl_3$): 7.41 ppm (d, 1H); 6.95 ppm (d, 1H); 6.45 ppm (s, 1H); 6.01 ppm (d, J=50Hz, 1H); 4.82 ppm (d, 2H); 4.78 ppm (s, 2H); 2.14 ppm (t, 1H).

Example P32: 1-Amino-3-(3-oxo-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazin-6-yl)-6-trifluoromethyl-1H-pyrimidine-2,4-dione

1.77 g (4.9 mmol) of 1-methylthio-3-(3-oxo-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazin-6-yl)-6-trifluoromethyl-1H-pyrimidine-2,4-dione (compound no. 2.002) is dissolved in 15 ml chloroform and treated with 2.44 g (9.8 mmol) m-chloroperbenzoic acid stirring and maintaining the temperature at below 30 °C. After 3 hours, according to thin layer chromatography the 1-methylsulfonyl-3-(3-oxo-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazin-6-yl)-6-trifluoromethyl-1H-pyrimidine-2,4-dione (compound no. 2.008) can be detected only, the reaction mixture is added under stirring to an ice-cold solution of 25% ammoniumhydroxide. After 5 minutes the crystals formed are filtered, washed with water and dried yielding

technical grade 1-amino-3-(3-oxo-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazin-6-yl)-6-trifluoromethyl-1H-pyrimidine-2,4-dione with a melting point of >250°C. ^{1}H-NMR ($(CD_3)_2SO$): 10.65 ppm (broad signal, NH); 7.38 ppm (d, 1H); 7.3 ppm (broad signal, NH_2); 6.92 ppm (d, 1H); 6.02 ppm, (s, 1H); 4.62 ppm (s, 2H).

Example P33: 6-(7-Oxo-5-trifluoromethyl-7H-imidazo[1,2-a]pyrimidin-8-yl)-4H-pyrido[3,2-b][1,4]oxazin-3-one

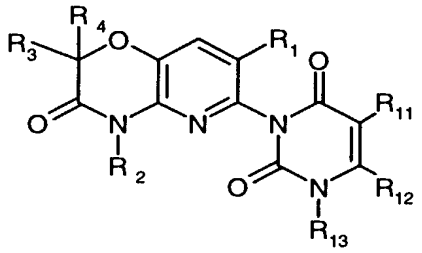
1.15 g (3.5 mmol) 1-amino-3-(3-oxo-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazin-6-yl)-6-trifluoromethyl-1H-pyrimidine-2,4-dione (Example P32) is added to a well-stirred mixture of 1 ml 32% hydrochloric acid and 5 ml acetic acid containing 1.12 g (7.0 mmol) bromoacetaldehyde and heated afterwards for 17 hours to refluxing temperature. The cold solution is acidified to pH 3 and extracted with ethylacetate. The organic phase is washed once with sodiumbicarbonate solution and evaporated. By HPLC the pure 6-(7-oxo-5-trifluoromethyl-7H-imidazo[1,2-a]pyrimidin-8-yl)-4H-pyrido[3,2-b][1,4]oxazin-3-one is obtained. ^{1}H-NMR ($(CD_3)_2SO$): 11.23 ppm (s, NH); 7.35 ppm (d, 1H); 7.32 ppm (b, 1H); 6.91 ppm (d, 1H); 6.88 ppm (b, 1H); 6.78 ppm (s, 1H); 4.53 ppm (s, 2H).

Example P34: 1,5-Dimethyl-3-(3-oxo-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazin-6-yl)-6-thioxo-[1,3,5]triazinane-2,4-dione

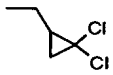
0.57 g (2 mmol) (3-oxo-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazin-6-yl)-carbamic acid phenyl ester (compound no. II.029) is added to a solution of 0.22 g (2 mmol) N,N'-dimethylthiourea in 10 ml NMP containing a catalytic amount of triethylamine. After 5 minutes 0.65 g (4 mmol) carbonyldiimidazole is added and the mixture heated for 6 hours to 80 °C. Then once again 0.65 g (4 mmol) carbonyldiimidazole is added and the mixture stirred further overnight at 95°C. The reaction mixture is poured into icewater and the crystals of almost pure 1,5-dimethyl-3-(3-oxo-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazin-6-yl)-6-thioxo-[1,3,5]triazinane-2,4-dione are filtered off and dried. ^{1}H-NMR ($(CD_3)_2SO$): 11.58 ppm (s, NH); 7.68 ppm (d, 1H); 7.22 ppm (d, 1H); 4.88 ppm (s, 2H); 3.72 ppm (s, 6H).

The preferred compounds listed in the following Tables 1, 2, 4, 5, 7, 11, 12 and 100 can also be obtained in analogous manner or using methods described in the Reaction Schemes and in the mentioned references.

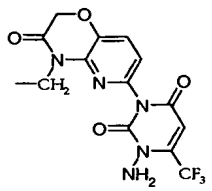
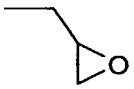
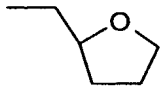
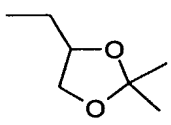
Table 1: Compounds of formula IW_{1a}



(IW_{1a})

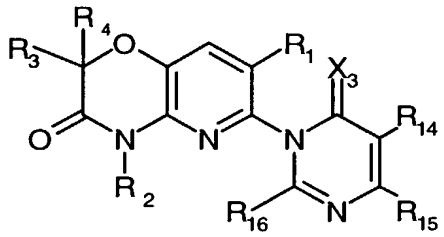
comp. no. (Example)	R_1	R_2	R_3	R_4	R_{11}	R_{12}	R_{13}	physical data
1.001 (P4)	H	H	H	H	H	CF_3	H	>220°C
1.002 (P6)	H	H	H	H	H	CF_3	CH_3	>220°C
1.003 (P5)	H	CH_3	H	H	H	CF_3	CH_3	211-212°C
1.004 (P8)	H	isopropyl	H	H	H	CF_3	CH_3	solid
1.005 (P7)	H	$CH_2C{\equiv}CH$	H	H	H	CF_3	CH_3	161-162°C
1.006	H	$CH_2C{\equiv}CH$	H	H	H	CF_3	H	183-184°C
1.007	H	$CH_2C{\equiv}CH$	H	H	H	CF_3	$CH_2C{\equiv}CH$	amorphous crystals
1.008	H	CH_2CH_3	H	H	H	CF_3	H	205-206°C
1.009	H	H	H	H	H	CF_3	CH_2CH_3	220°C
1.010	H	CH_2CH_3	H	H	H	CF_3	CH_2CH_3	resin
1.011	H	$CH_2C{\equiv}CH$	H	H	H	CF_3	CH_2CH_3	169-170°C
1.012	H	CH_2CH_3	H	H	H	CF_3	CH_3	191-192°C
1.013	H	$CH_2CH{=}CH_2$	H	H	H	CF_3	CH_3	133-135°C
1.014	H	isobutyl	H	H	H	CF_3	CH_3	resin
1.015	H	sec-butyl	H	H	H	CF_3	CH_3	amorphous crystals
1.016	H	$CH(CH_3)C{\equiv}CH$	H	H	H	CF_3	CH_3	amorphous crystals
1.017	H	$CH_2C{\equiv}N$	H	H	H	CF_3	CH_3	208-209°C
1.018	H	$CH_2CH_2OCH_3$	H	H	H	CF_3	CH_3	154-155°C
1.019	H	$CH_2CCl{=}CH_2$	H	H	H	CF_3	CH_3	amorphous crystals
1.020	H	$CH(CH_3)CH{=}CH_2$	H	H	H	CF_3	CH_3	amorphous crystals
1.021	H	CH_2SCH_3	H	H	H	CF_3	CH_3	resin
1.022	H		H	H	H	CF_3	CH_3	resin
1.023	H	$CH_2CH{=}CHCH_3$	H	H	H	CF_3	CH_3	amorphous crystals
1.024	H		H	H	H	CF_3	CH_3	109-110°C, 166-167°C (dual melting point)
1.025	H	$CH_2CH_2CH(OCH_3)_2$	H	H	H	CF_3	CH_3	resin
1.026	H	3-MeO-benzyl	H	H	H	CF_3	CH_3	resin
1.027	H	$CH_2C(CH_3){=}CH_2$	H	H	H	CF_3	CH_3	144-145°C
1.028	H	$CH_2C(O)OCH_2CH_2OCH_3$	H	H	H	CF_3	CH_3	resin
1.029	H	4-Cl-benzyl	H	H	H	CF_3	CH_3	amorphous crystals
1.030	H	4-benzyloxy-benzyl	H	H	H	CF_3	CH_3	resin
1.031	H	3-phenoxy-benzyl	H	H	H	CF_3	CH_3	resin
1.032	H	$CH_2CH{=}C(CH_3)Cl$	H	H	H	CF_3	CH_3	resin
1.033	H	$CH_2CH_2CH_2Cl$	H	H	H	CF_3	CH_3	resin

1.034	H	$CH_2CH_2CH_2CH_2Cl$	H	H	H	CF_3	CH_3	resin
1.035	H	$CH_2CH(CH_3)CH_2Cl$	H	H	H	CF_3	CH_3	resin
1.036	H	$CH_2C(O)OC(CH_3)_3$	H	H	H	CF_3	CH_3	resin
1.037	H	4-MeO-benzyl	H	H	H	CF_3	CH_3	amorphous crystals
1.038	H	$CH_2C(O)C(CH_3)_3$	H	H	H	CF_3	CH_3	resin
1.039	H	2-Cl-benzyl	H	H	H	CF_3	CH_3	resin
1.040	H	$CH_2CH_2CF=CF_2$	H	H	H	CF_3	CH_3	amorphous crystals
1.041	H	$CH_2CH_2CH_2F$	H	H	H	CF_3	CH_3	resin
1.042	H	$CH_2CH=CHC\equiv CC(CH_3)_3$	H	H	H	CF_3	CH_3	resin
1.043	H	CH_2CH_2-phenyl	H	H	H	CF_3	CH_3	amorphous crystals
1.044	H	H	n-butyl	H	H	CF_3	H	>225°C
1.045	H	H	CH_2CH_3	H	H	CF_3	H	>225°C
1.046	H	H	CH_3	H	H	CF_3	H	>225°C
1.047	H	H	CH_3	H	H	CF_3	CH_3	>230°C
1.048	H	H	CH_2CH_3	H	H	CF_3	CH_3	>230°C
1.049	H	H	n-butyl	H	H	CF_3	CH_3	208-209°C
1.049	H	CH_2CH_3	n-butyl	H	H	CF_3	CH_3	resin
1.050	H	$CH_2C\equiv CH$	n-butyl	H	H	CF_3	CH_3	122-123°C
1.051	H	$CH_2CH=CH_2$	n-butyl	H	H	CF_3	CH_3	102-103°C
1.052	H	$CH_2CH=CH_2$	CH_2CH_3	H	H	CF_3	CH_3	75-76°C
1.053	H	$CH_2C\equiv CH$	CH_2CH_3	H	H	CF_3	CH_3	109-110°C
1.054	H	$CH_2C\equiv CH$	CH_3	H	H	CF_3	CH_3	79-80°C
1.055	H	$CH_2CH=CH_2$	CH_3	H	H	CF_3	CH_3	115-116°C
1.056	H	CH_2CH_3	CH_3	H	H	CF_3	CH_3	135-136°C
1.057	H	$CH(CH_3)_2$	CH_3	H	H	CF_3	CH_3	104-105°C
1.058	H	$CH_2CH_2CH_3$	CH_3	H	H	CF_3	CH_3	110-111°C
1.059	H	CH_2CF_3	CH_3	H	H	CF_3	CH_3	180-181°C
1.060	H	$CH_2CH_2CH_3$	H	H	H	CF_3	CH_3	146-147°C
1.061	H	$CH_2CH_2CH_2=CH_2$	H	H	H	CF_3	CH_3	143-144°C
1.062 (P20)	H	H	H	H	H	CF_3	NH_2	>220°C
1.063	H	$CH_2C\equiv CH$	H	H	H	CF_3	NH_2	114-115°C
1.064	H	$CH_2CH=CH_2$	H	H	H	CF_3	NH_2	94°C
1.065	H	CH_2CF_3	H	H	H	CF_3	CH_3	resin
1.066	H	CH_2CH_3	H	H	H	CF_3	NH_2	165-167°C
1.067	H	CH_3	H	H	H	CF_3	NH_2	> 220°C
1.068	H	$CH(CH_3)C\equiv CH$	H	H	H	CF_3	NH_2	89°C (decomposition)
1.069	H	$CH_2CH_2CH_3$	H	H	H	CF_3	NH_2	amorphous crystals
1.070	H	$CH_2C(O)CH_2CH_3$	H	H	H	CF_3	NH_2	163-164°C
1.071	H	$CH_2C(O)CH_2CH_3$	H	H	H	CF_3	CH_3	203-204°C
1.072	H	$CH_2C(O)$-cyclopropyl	H	H	H	CF_3	CH_3	202-203°C
1.073	H	$CH_2CH(OCH_3)_2$	H	H	H	CF_3	CH_3	177-178°C
1.074	H	CH_2CH_2Cl	H	H	H	CF_3	CH_3	154-155°C
1.075	H	$CH_2C(O)C(CH_3)_3$	H	H	H	CF_3	NH_2	resin
1.076	H	$CH_2C(O)OC(CH_3)_3$	H	H	H	CF_3	NH_2	resin
1.077	H	$CH_2CH=CH(Cl)CH_3$	H	H	H	CF_3	NH_2	resin
1.078	H	$CH_2CH_2CH_2Cl$	H	H	H	CF_3	NH_2	resin
1.079	H	$CH_2CH_2CH_2CH_2CH_2Cl$	H	H	H	CF_3	NH_2	resin

1.080	H		H	H	H	CF_3	NH_2	amorphous crystals
1.081	H	$CH_2Si(CH_3)_2CH_2CH_3$	H	H	H	CF_3	NH_2	resin
1.082	H	$CH_2CH_2CH_2CH_2Cl$	H	H	H	CF_3	NH_2	resin
1.083	H	$CH_2CH(CH_3)CH_2Cl$	H	H	H	CF_3	NH_2	resin
1.084	H	$CH_2CH_2CH_2CH=CH_2$	H	H	H	CF_3	NH_2	resin
1.085	H	$CH_2CH_2CH_2F$	H	H	H	CF_3	NH_2	147.5-148°C
1.086	H	$CH_2C(CH_2Si(CH_3)_3)=CH_2$	H	H	H	CF_3	NH_2	resin
1.087	H	$CH_2CH=CHC\equiv CC(CH_3)_3$	H	H	H	CF_3	NH_2	resin
1.088	H	$CH_2C(Br)=CH_2$	H	H	H	CF_3	NH_2	resin
1.089	H	$CH(CH_2CH_3)C(O)OCH_3$	H	H	H	CF_3	NH_2	resin
1.090	H		H	H	H	CF_3	NH_2	resin
1.091	H	$CH_2CH_2CH(CH_3)_2$	H	H	H	CF_3	NH_2	resin
1.092	H		H	H	H	CF_3	NH_2	resin
1.093	H	$CH_2CH_2CH_2C\equiv N$	H	H	H	CF_3	NH_2	resin
1.094	H	$CH_2CH_2OCH_2CH_2OCH_3$	H	H	H	CF_3	NH_2	amorphous crystals
1.095	H	$CH_2CH=CHCH_3$	H	H	H	CF_3	NH_2	amorphous crystals
1.096	H	$CH_2CH=CHC(O)OCH_3$	H	H	H	CF_3	NH_2	resin
1.097	H	$CH_2C(CH_3)=CH_2$	H	H	H	CF_3	NH_2	resin
1.098	H	$CH_2CH_2CH=C(CH_3)_2$	H	H	H	CF_3	NH_2	amorphous crystals
1.099	H	$CH_2CH_2CH_2C\equiv CH$	H	H	H	CF_3	NH_2	resin
1.100	H	n-nonyl	H	H	H	CF_3	NH_2	resin
1.101	H	$CH_2CH_2CH(Cl)CH_3$	H	H	H	CF_3	NH_2	resin
1.102	H		H	H	H	CF_3	NH_2	resin
1.103	H	$CH_2CH(CH_2CH_3)_2$	H	H	H	CF_3	NH_2	resin
1.104	H	CH_2CHF_2	H	H	H	CF_3	NH_2	resin
1.105	H		H	H	H	CF_3	NH_2	resin
1.106	H	cyclohexyl	H	H	H	CF_3	NH_2	resin
1.107 (P30)	H	$CH_2CH_2CH_3$	H	H	Cl	CF_3	CH_3	110-111°C

1.108	H	$CH(CH_3)_2$	H	H	H	CF_3	NH_2	^{1}H-NMR ($CDCl_3$): 7.37 ppm (d, 1H); 6.88 ppm (d, 1H); 6.28 ppm (s, 1H); 5.18 ppm (q, 1H); 4.62 ppm (s, 2H); 4.58 ppm (NH_2); 1.51 ppm (d, 6H).
1.109 (P31)	H	$CH_2C{\equiv}CH$	H	H	H	CF_3	CH_2F	191-193°C
1.110	H	$CH_2CH_2CH_2CH_3$	H	H	H	CF_3	CH_3	147-148°C
1.111	H	$CH_2CH{=}C(CH_3)_2$	H	H	H	CF_3	CH_3	141-142°C
1.112	H	$CH_2CH{=}CHCH_2CH_3$	H	H	H	CF_3	CH_3	141-142°C, <Z>-isomer
1.113	H	$CH_2CH{=}CHCH_2CH_3$	H	H	H	CF_3	CH_3	141-142°C, <E>-isomer
1.114	H	$CH_2CH_2CH_2CH{=}CH_2$	H	H	H	CF_3	CH_3	154°C

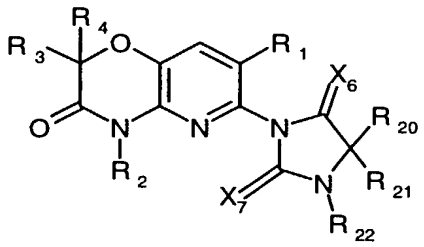
Table 2: Compounds of formula IW_2



(IW_2)

comp. no. (Example)	R_1	R_2	R_3	R_4	X_3	R_{14}	R_{15}	R_{16}	physical data, remarks
2.001 (P22)	H	H	H	H	O	H	CF_3	SH	>220°C, tautomeric form IW_{1g}
2.002	H	H	H	H	O	H	CF_3	SCH_3	>206°C
2.003	H	CH_3	H	H	O	H	CF_3	SCH_3	>220°C
2.004	H	$CH_2CH{=}CH_2$	H	H	O	H	CF_3	SCH_3	143-144°C
2.005	H	$CH_2C{\equiv}CH$	H	H	O	H	CF_3	SCH_3	183-184°C
2.006	H	$CH_2CH_2CH_3$	H	H	O	H	CF_3	SCH_3	128-129°C
2.007 (P31)	H	$CH_2C{\equiv}CH$	H	H	O	H	CF_3	OCH_2F	resin
2.008	H	H	H	H	O	H	CF_3	SO_2CH_3	^{1}H-NMR (DMSO-D_6): 11.41 ppm (s, 1H); 7.45 ppm (d, 1H); 7.37 ppm (s, 1H); 7.07 ppm (d, 1H); 4.67 ppm (s, 2H); 3.32 ppm (s, 3H).
2.009 (P32)	H	H	H	H	O	H	CF_3	NH_2	>250°C

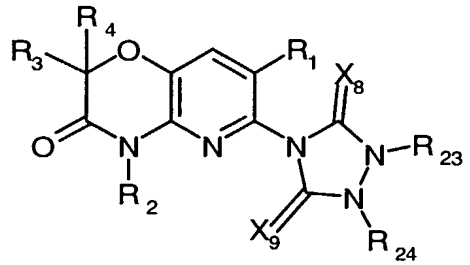
Table 4: Compounds of formula IW_4



(IW_4)

comp. no. (Example)	R_1	R_2	R_3	R_4	X_6	X_7	R_{20}	R_{21} R_{22}	physical data
4.001	H	H	H	H	O	O	H	$-CH_2CH(OH)CH_2CH_2-$	225°C (isomer I)
4.002	H	H	H	H	O	O	H	$-CH_2CH(OH)CH_2CH_2-$	225°C (isomer II)
4.003 (P18)	H	$CH_2C\equiv CH$	H	H	O	O	H	$-CH_2CH(OH)CH_2CH_2-$	205.5-206°C
4.004 (P19)	H	$CH_2C\equiv CH$	H	H	O	O	H	$-CH_2CH(F)CH_2CH_2-$	205°C (isomer I)
4.005 (P19)	H	$CH_2C\equiv CH$	H	H	O	O	H	$-CH_2CH(F)CH_2CH_2-$	205°C (isomer II)

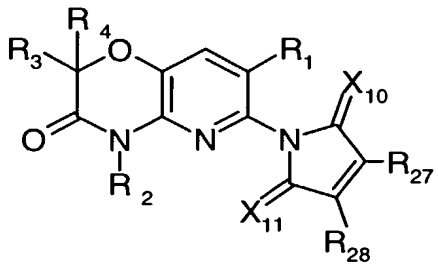
Table 5: Compounds of formula IW_5



(IW_5)

comp. no. (Example)	R_1	R_2	R_3	R_4	X_8	X_9	R_{23} R_{24}	physical data
5.001 (P24)	H	H	H	H	S	O	$-CH_2CH_2CH_2CH_2-$	>225°C
5.002 (P25)	H	$CH_2C\equiv CH$	H	H	S	O	$-CH_2CH_2CH_2CH_2-$	>225°C
5.003	H	$CH_2CH=CH_2$	H	H	S	O	$-CH_2CH_2CH_2CH_2-$	186-187°C
5.004	H	$CH_2CH_2CH_3$	H	H	S	O	$-CH_2CH_2CH_2CH_2-$	210-210.5°C
5.005	H	CH_2CH_3	H	H	S	O	$-CH_2CH_2CH_2CH_2-$	197-197.5°C
5.006	H	H	H	H	S	O	$-CH_2CH_2OCH_2CH_2-$	>225°C
5.007	H	$CH_2CH=CH_2$	H	H	S	O	$-CH_2CH_2OCH_2CH_2-$	192-193°C
5.008	H	$CH_2C\equiv CH$	H	H	S	O	$-CH_2CH_2OCH_2CH_2-$	>225°C
5.009	H	$CH_2CH_2CH_3$	H	H	S	O	$-CH_2CH_2OCH_2CH_2-$	172-173°C
5.010	H	CH_2CH_3	H	H	S	O	$-CH_2CH_2OCH_2CH_2-$	223-224°C
5.011	H	$CH_2CH_2CH_2CH_3$	H	H	S	O	$-CH_2CH_2CH_2CH_2-$	153-154°C
5.012	H	$CH_2CH_2CH=CH_2$	H	H	S	O	$-CH_2CH_2CH_2CH_2-$	153-154°C
5.013	H	$CH_2CH_2CH_2CH=CH_2$	H	H	S	O	$-CH_2CH_2CH_2CH_2-$	177-178°C

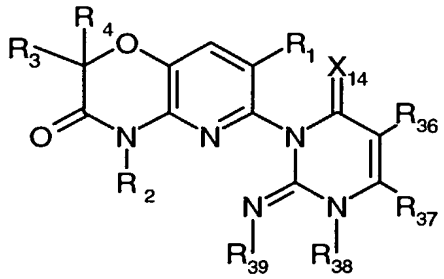
Table 7: Compounds of formula IW_7



(IW_7)

comp. no. (Example)	R_1	R_2	R_3	R_4	R_{27} R_{28}	X_{10}	X_{11}	physical data
7.001	H	$CH_2C\equiv CH$	H	H	$-CH_2CH_2CH_2CH_2-$	O	O	181-182°C
7.002	H	$CH(CH_3)C\equiv CH$	H	H	$-CH_2CH_2CH_2CH_2-$	O	O	69-70°C
7.003	H	isopropyl	H	H	$-CH_2CH_2CH_2CH_2-$	O	O	137-138°C
7.004	H	$CH_2CH=CHCl$ (cis)	H	H	$-CH_2CH_2CH_2CH_2-$	O	O	resin
7.005	H	$CH_2CH=CHCl$ (trans)	H	H	$-CH_2CH_2CH_2CH_2-$	O	O	141-142°C
7.006	H	benzyl	H	H	$-CH_2CH_2CH_2CH_2-$	O	O	178-179°C
7.007 (P15)	H	H	H	H	$-CH_2CH_2CH_2CH_2-$	O	O	220°C
7.008	H	H	H	H	-CH=CH-CH=CH-	O	O	>220°C
7.009	H	$CH_2C\equiv CH$	H	H	-CH=CH-CH=CH-	O	O	>220°C
7.010	H	$CH_2CH=CH_2$	H	H	-CH=CH-CH=CH-	O	O	183-184°C

Table 11: Compounds of formula IW_{11}



(IW_{11})

comp. no. (Example)	R_1	R_2	R_3	R_4	X_{14}	R_{36}	R_{37}	R_{38} R_{39}	physical data, remarks
11.001 (P28)	H	H	H	H	O	H	CF_3	$-CH_2CH_2-$	>225°C
11.002	H	H	H	H	O	H	CF_3	$-CH_2CH(CH_3)-$	>225°C
11.003	H	$CH_2C\equiv CH$	H	H	O	H	CF_3	$-CH_2CH_2-$	223-224°C
11.004	H	$CH_2CH=CH_2$	H	H	O	H	CF_3	$-CH_2CH_2-$	152-153°C
11.005	H	$CH_2CH_2CH_3$	H	H	O	H	CF_3	$-CH_2CH_2-$	137-137.5°C
11.006	H	CH_2CH_3	H	H	O	H	CF_3	$-CH_2CH_2-$	159.5-160°C
11.007	H	$CH(CH_3)C\equiv CH$	H	H	O	H	CF_3	$-CH_2CH_2-$	206.5-207.5°C
11.008	H	$CH_2C\equiv CH$	H	H	O	H	CF_3	$-CH_2CH(CH_3)-$	191-191.5°C
11.009	H	$CH_2CH=CH_2$	H	H	O	H	CF_3	$-CH_2CH(CH_3)-$	143-143.5°C
11.010	H	CH_2CH_3	H	H	O	H	CF_3	$-CH_2CH(CH_3)-$	115-117°C, 126-128°C (dual melting point)
11.011	H	$CH_2CH_2CH_3$	H	H	O	H	CF_3	$-CH_2CH(CH_3)-$	122-122.5°C

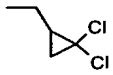
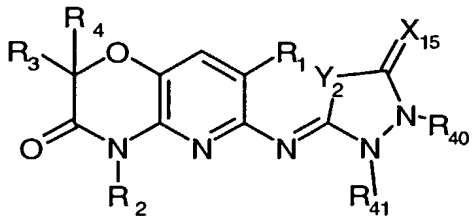
11.012 (P29)	H	$CH(CH_3)C\equiv CH$	H	H	O	H	CF_3	$-CH_2CH(CH_3)-$	resin, isomer I
11.013 (P29)	H	$CH(CH_3)C\equiv CH$	H	H	O	H	CF_3	$-CH_2CH(CH_3)-$	>200°C (decomp.), isomer II
11.014	H	$CH_2C(O)C(CH_3)_3$	H	H	O	H	CF_3	$-CH_2CH_2-$	resin
11.015	H	$CH_2C(O)OC(CH_3)_3$	H	H	O	H	CF_3	$-CH_2CH_2-$	resin
11.016	H	$CH_2CH=C(Cl)CH_3$	H	H	O	H	CF_3	$-CH_2CH_2-$	resin, <E>/<Z>-mixture
11.017	H	$CH_2CH_2CH_2Cl$	H	H	O	H	CF_3	$-CH_2CH_2-$	resin
11.018	H	$CH_2CH_2CH_2CH_2CH_2Cl$	H	H	O	H	CF_3	$-CH_2CH_2-$	resin
11.019	H	$CH_2Si(CH_3)_2CH_2CH_3$	H	H	O	H	CF_3	$-CH_2CH_2-$	resin
11.020	H	$CH_2CH(CH_3)CH_2Cl$	H	H	O	H	CF_3	$-CH_2CH_2-$	resin
11.021	H	$CH_2CH_2CH_2CH=CH_2$	H	H	O	H	CF_3	$-CH_2CH_2-$	resin
11.022	H	$CH_2CH_2CH_2F$	H	H	O	H	CF_3	$-CH_2CH_2-$	resin
11.023	H	$CH_2C(=CH_2)CH_2Si(CH_3)_3$	H	H	O	H	CF_3	$-CH_2CH_2-$	resin
11.024	H	$CH_2CH=CHC\equiv CC(CH_3)_3$	H	H	O	H	CF_3	$-CH_2CH_2-$	resin
11.025	H	$CH_2C(O)CH_2CH_3$	H	H	O	H	CF_3	$-CH_2CH_2-$	resin
11.026	H	$CH_2C(Br)=CH_2$	H	H	O	H	CF_3	$-CH_2CH_2-$	resin
11.027	H	$CH_2CH(COOCH_3)CH_2CH_3$	H	H	O	H	CF_3	$-CH_2CH_2-$	resin
11.028	H		H	H	O	H	CF_3	$-CH_2CH_2-$	resin
11.029	H	$CH_2CH_2CH(CH_3)_2$	H	H	O	H	CF_3	$-CH_2CH_2-$	resin
11.030	H		H	H	O	H	CF_3	$-CH_2CH_2-$	resin
11.031	H	$CH_2CH_2CH_2C\equiv N$	H	H	O	H	CF_3	$-CH_2CH_2-$	resin
11.032	H	$CH_2CH_2OCH_2CH_2OCH_3$	H	H	O	H	CF_3	$-CH_2CH_2-$	resin
11.033	H	$CH(CH_3)CH=CH_2$	H	H	O	H	CF_3	$-CH_2CH_2-$	resin
11.034	H	$CH_2CH=CHCOOCH_3$	H	H	O	H	CF_3	$-CH_2CH_2-$	resin
11.035	H	$CH_2C(CH_3)=CH_2$	H	H	O	H	CF_3	$-CH_2CH_2-$	resin
11.036	H	$CH_2CH_2CH=C(CH_3)_2$	H	H	O	H	CF_3	$-CH_2CH_2-$	resin
11.037 (P33)	H	H	H	H	O	H	CF_3	-CH=CH-	>225°C
11.038	H	$CH_2C\equiv CH$	H	H	O	H	CF_3	-CH=CH-	208-210 °C

Table 12: Compounds of formula IW_{12}

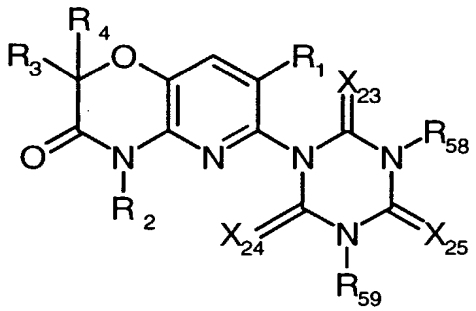


(IW_{12})

comp. no. (Example)	R_1	R_2	R_3	R_4	Y_2	X_{15}	R_{40}	R_{41}	physical data
12.001 (P24)	H	H	H	H	S	O	$-CH_2CH_2CH_2CH_2-$		>225°C, <E> or <Z> isomer
12.002 (P25)	H	$CH_2C\equiv CH$	H	H	S	O	$-CH_2CH_2CH_2CH_2-$		>225°C, <E> or <Z> isomer
12.003	H	$CH_2CH=CH_2$	H	H	S	O	$-CH_2CH_2CH_2CH_2-$		197-198°C, <E> or <Z> isomer
12.004	H	$CH_2CH_2CH_3$	H	H	S	O	$-CH_2CH_2CH_2CH_2-$		188-189°C, <E> or <Z> isomer

12.005	H	CH_2CH_3	H	H	S	O	$-CH_2CH_2CH_2CH_2-$	>220°C, <E> or <Z> isomer
12.006	H	H	H	H	S	O	$-CH_2CH_2OCH_2CH_2-$	>225°C, <E> or <Z> isomer
12.007	H	$CH_2CH=CH_2$	H	H	S	O	$-CH_2CH_2OCH_2CH_2-$	221-22°C,<E> or <Z> isomer
12.008	H	$CH_2C\equiv CH$	H	H	S	O	$-CH_2CH_2OCH_2CH_2-$	>225°C, <E> or <Z> isomer
12.009	H	$CH_2CH_2CH_3$	H	H	S	O	$-CH_2CH_2OCH_2CH_2-$	214-215°C, <E> or <Z> isomer
12.010	H	$CH_2CH_2CH_2CH_3$	H	H	S	O	$-CH_2CH_2CH_2CH_2-$	129-130°C, <E> or <Z> isomer
12.011	H	$CH_2CH_2CH=CH_2$	H	H	S	O	$-CH_2CH_2CH_2CH_2-$	154-165°C, <E> or <Z> isomer
12.012	H	$CH_2CH_2CH_2CH=CH_2$	H	H	S	O	$-CH_2CH_2CH_2CH_2$	141-142°C, <E> or <Z> isomer

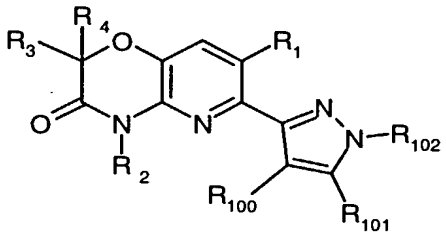
Table 21: Compounds of formula IW_{21}



(IW_{21})

comp. no. (Example)	R_1	R_2	R_3	R_4	X_{23}	X_{24}	X_{25}	R_{58}	R_{59}	physical data
21.001 (P34)	H	H	H	H	O	O	S	CH_3	CH_3	>225°C
21.002	H	$CH_2C\equiv CH$	H	H	O	O	S	CH_3	CH_3	
21.003	H	$CH_2CH=CH_2$	H	H	O	O	S	CH_3	CH_3	

Table 100: Compounds of formula IW_{100}

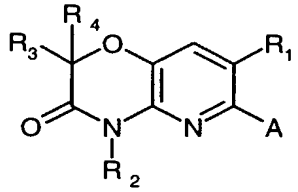


(IW_{100})

comp. no. (Example)	R_1	R_2	R_3	R_4	R_{100}	R_{101}	R_{102}	physical data
100.001	F	$CH_2C\equiv CH$	H	H	Cl	$OCHF_2$	CH_3	127-128°C
100.002	F	CH_3	H	H	Cl	$OCHF_2$	CH_3	138-139°C
100.003 (P9)	F	H	H	H	Cl	$OCHF_2$	CH_3	solid
100.004	F	isopropyl	H	H	Cl	$OCHF_2$	CH_3	123-124°C
100.005	F	$CH(CH_3)COOCH_3$	H	H	Cl	$OCHF_2$	CH_3	93-95°C
100.006	F	$CH_2CH_2SCH_2CH_3$	H	H	Cl	$OCHF_2$	CH_3	oil

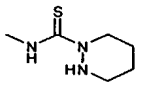
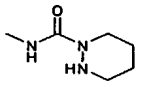
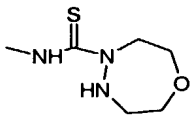
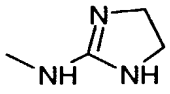
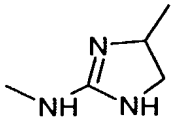
100.007 (P13)	H	H	H	CH_3	H	$OCHF_2$	CH_3	solid
100.008 (P14)	H	H	H	CH_3	Cl	$OCHF_2$	CH_3	solid
100.009 (P12)	H	H	H	CH_3	H	OH	CH_3	solid; tautomeric form IW_{100z}

Table II: Compounds of formula II:



(II)

comp. no. (Example)	R_1	R_2	R_3	R_4	A	physical data
II.001 (P1)	H	H	H	H	NO_2	247-252°C
II.002 (P2)	H	H	H	H	NH_2	279-281°C
II.003 (P21)	H	H	H	H	N=C=S	178-179°C
II.004	Br	H	H	H	NO_2	solid
II.005	Cl	H	H	H	Cl	solid
II.006	Cl	H	H	H	NO_2	206-207°C
II.007	H	H	CH_3	H	NO_2	186-187°C
II.008	H	H	n-butyl	H	NO_2	solid
II.009	H	H	CH_3	H	N=C=S	solid
II.010	H	H	n-butyl	H	NH_2	>235°C
II.011	H	H	n-butyl	H	N=C=S	solid
II.012	H	H	n-butyl	H	$NHCSNHC(CH_3)_3$	solid
II.013	H	H	CH_3	H	NH_2	>230°C
II.014	H	H	H	H	$NHCSNHC(CH_3)_3$	solid
II.015	H	H	n-decyl	H	N=C=S	solid
II.016	Cl	H	n-butyl	H	NO_2	solid
II.017	H	H	CH_2CH_3	H	CH_3	solid
II.018	H	H	CH_3	CH_3	CH_3	solid
II.019	Cl	H	CH_2CH_3	H	CH_3	solid
II.020	Cl	H	CH_3	H	CH_3	solid
II.021	Cl	H	CH_3	CH_3	CH_3	solid
II.022	Cl	H	n-butyl	H	N=C=S	solid
II.023	H	H	2,4-Cl_2-6-NO_2-phenyl	H	NO_2	solid
II.024	H	H	H	H	Br	solid
II.025 (P10)	H	H	H	H	COOH	138-140°C
II.026	H	H	CH_3	H	COOH	H-NMR ($(CD_3)_2SO$)): 11.80 ppm (s, NH); 7.68 ppm (d, 1H); 7.45 ppm (d, 1H); 4.88 ppm (q, 1H); 1.47 ppm (d, 3H).
II.027 (P11)	H	H	CH_3	H	$COCH_2COOEt$	oil
II.028	Br	H	H	H	NH_2	220°C
II.029	H	H	H	H	NHCOO-phenyl	>225°C
II.030 (P16)	H	$CH_2C{\equiv}CH$	H	H	NH_2	125-126°C

II.031	(P17)	H	$CH_2C{\equiv}CH$	H	H	N=C=O	amorphous crystals
II.032	(P17)	H	$CH_2C{\equiv}CH$	H	H	NHCOOMe	amorphous crystals
II.033	(P3)	H	H	H	H	NHCOOEt	220°C
II.034		Cl	H	H	H	NH_2	>230°C
II.035		H	H	H	H	Cl	180-181°C
II.036		H	$CH_2C{\equiv}CH$	H	H	NHCOOEt	154-155°C
II.037		H	H	CH_3	H	NHCOOEt	>220°C
II.038		H	H	CH_2CH_3	H	NHCOOEt	>225°C
II.039		H	H	n-butyl	H	NHCOOEt	>220°C
II.040		Cl	H	H	H	$NHCOOC(CH_3)_3$	amorphous crystals
II.041		H	CH_2CH_3	H	H	NH_2	95°C
II.042		H	$CH_2CH{=}CH_2$	H	H	NH_2	91°C
II.043		H	$CH_2CH{=}CH_2$	H	H	NHCOOEt	100-101°C
II.044		H	H	H	H	$NHCOOCH_2CH(CH_3)_2$	232-234°C
II.045		H	$CH_2CH{=}CH_2$	H	H	OH	112-113°C
II.046		H	CH_2CF_3	H	H	NH_2	resin
II.047		H	CH_2CF_3	H	H	NHCOOEt	resin
II.048	(P23)	H	H	H	H		212-212.5°C
II.049		H	H	H	H		> 220°C
II.050		H	H	H	H		212.5-213°C
II.051	(P26)	H	H	H	H	NHC(S)OEt	218-219°C
II.052	(P27)	H	H	H	H		>225°C
II.053		H	H	H	H		>225°C
II.054		H	$CH_2C{\equiv}CH$	H	H	N=C=S	135-136°C
II.055		Br	H	H	H	Br	230-232°C
II.056		Br	CH_2CH_3	H	H	Br	115-116°C
II.057		H	CH_2CH_3	H	H	Cl	76-77°C
II.058		H	H	CH_2CH_3	H	NO_2	182-183°C
II.059		H	H	CH_2CH_3	H	NH_2	231-232°C

Biological Examples:

Example B1: Herbicidal action before emergence of the plants (pre-emergence action)

Monocotyledonous and dicotyledonous test plants are sown in standard soil in plastics pots. Immediately after sowing, the test compounds, in the form of an aqueous suspension (prepared from a 25 % wettable powder (Example F3, b) according to WO 97/34485), or in the form of an emulsion (prepared from a 25 % emulsifiable concentrate (Example F1, c) according to WO 97/34485), are applied by spraying in a concentration corresponding to 250 g of active ingredient/ha (500 litres water/ha). The test plants are then grown in a greenhouse under optimum conditions. After a test duration of 3 weeks, the test is evaluated in accordance with a scale of nine ratings (1 = total damage, 9 = no action). Ratings of from 1 to 4 (especially from 1 to 3) indicate good to very good herbicidal action.

Test plants: Setaria, Panicum, Digitaria, Sida, Ipomea, Amaranthus, Chenopodium, Stellaria, Veronica.

The compounds according to the invention exhibit good herbicidal action.
Examples of the good herbicidal action of compounds of formula I are given in Table B1.

Table B1: Pre-emergence action (at 250 g a.i./ha)

comp. no.	Setaria	Panicum	Digitaria	Sida	Ipomea	Amaranthus	Chenopodium	Stellaria	Veronica
100.001	1	1	1	2	4	1	1	1	1
100.002	1	1	2	5	5	1	1	4	5
100.003	1	1	1	3	2	1	2	1	1
100.004	6	2	2	2	4	1	1	1	1
100.005	2	1	2	2	6	1	1	4	4
1.002	5	2	6	2	1	3	1	4	1
1.003	2	1	2	1	1	1	1	2	1
1.004	2	1	1	1	1	1	1	1	1
1.005	1	1	1	1	1	1	1	1	1
1.012	1	1	1	1	2	1	1	1	1
1.013	1	1	1	1	1	1	1	1	1
1.014	1	1	1	1	2	1	1	4	1
1.015	1	1	1	1	1	1	1	1	1
1.016	1	1	1	1	1	1	1	1	1
1.017	3	1	3	2	1	1	1	7	1
1.018	1	1	1	1	2	1	1	1	1
1.019	3	3	1	1	1	1	1	4	1
1.023	2	1	1	3	3	1	2	3	3
1.024	1	1	1	1	2	1	1	1	1
1.027	1	1	1	1	1	1	1	4	1
1.034	2	1	2	3	4	1	1	7	1
1.035	2	1	3	4	5	1	1	5	1
1.041	1	1	1	1	1	1	1	5	1

1.052	1	1	1	1	3	1	4	5	1
1.053	1	1	1	1	1	1	1	4	1
1.054	1	1	1	1	1	1	1	1	1
1.055	1	1	1	1	1	1	1	5	1
1.056	1	1	1	1	1	1	1	1	1
1.057	1	1	1	1	1	1	1	1	1
1.058	1	1	1	1	2	1	1	1	1
1.059	1	1	1	1	1	1	1	5	1
1.060	1	1	1	1	1	1	1	1	1
1.061	2	2	1	1	2	1	3	3	1
1.063	1	1	1	1	1	1	1	1	1
1.064	1	1	1	1	1	1	1	1	1
1.065	1	1	1	1	1	1	1	4	1
1.066	1	1	1	1	1	1	1	1	1
1.067	1	1	1	1	1	1	1	1	1
1.068	1	1	1	1	1	1	1	1	1
1.069	1	1	1	1	1	1	1	1	1
1.070	1	1	1	1	1	1	1	1	1
1.071	1	1	1	1	1	1	1	1	1

The same results are obtained when the compounds of formula I are formulated in accordance with Examples F2 and F4 to F8 according to WO 97/34485.

Example B2: Post-emergence herbicidal action

In a greenhouse, monocotyledonous and dicotyledonous test plants are grown in standard soil in plastics pots and at the 4- to 6-leaf stage are sprayed with an aqueous suspension of the test compounds of formula I, prepared from a 25 % wettable powder (Example F3, b) according to WO 97/34485), or with an emulsion of the test compounds of formula I, prepared from a 25 % emulsifiable concentrate (Example F1, c) according to WO 97/34485), in a concentration corresponding to 250 g of active ingredient/ha (500 litres water/ha). The test plants are then grown on in a greenhouse under optimum conditions. After a test duration of about 18 days, the test is evaluated in accordance with a scale of nine ratings (1 = total damage, 9 = no action). Ratings of from 1 to 4 (especially from 1 to 3) indicate good to very good herbicidal action.

Test plants: Setaria, Panicum, Digitaria, Euphorbia, Ipomea, Amaranthus, Chenopodium, Polygonum, Veronica.

In this test too, the compounds of formula I exhibit strong herbicidal action.

Examples of the good herbicidal action of compounds of formula I are given in Table B2.

Table B2: Post-emergence action (at 250 g of a.i./ha)

comp. no.	Setaria	Panicum	Digitaria	Euphorbia	Ipomea	Amaranthus	Chenopodium	Polygonum	Veronica
100.001	2	1	4	1	1	1	1	1	1
100.002	2	2	4	2	1	1	2	1	1
100.003	2	1	2	1	1	1	1	1	1
100.004	4	5	6	1	1	3	2	1	1
100.005	4	1	3	1	1	2	1	1	1
100.006	3	2	4	1	1	1	2	1	1
1.003	2	1	2	2	1	1	1	2	1
1.004	1	1	1	1	1	1	1	1	1
1.005	1	1	1	1	1	1	1	1	1
7.001	2	1	2	1	1	1	1	1	1
7.002	1	1	1	1	1	1	1	2	1
7.003	5	1	7	1	1	1	1	1	1
7.004	7	2	8	2	1	1	1	1	1
4.004	9	4	8	2	1	1	1	1	1
1.012	1	1	1	2	1	1	1	1	1
1.013	1	1	1	2	1	1	1	1	1
1.014	2	1	1	2	1	1	1	1	1
1.015	1	1	1	2	1	1	1	1	1
1.016	2	1	2	2	1	1	1	1	1
1.017	6	1	3	2	1	1	1	1	1
1.018	2	1	2	2	1	1	1	1	1
1.019	3	1	2	3	1	1	1	-	1
1.020	2	1	1	1	1	1	1	-	1
1.022	1	1	1	1	1	1	1	-	1
1.023	1	1	1	2	1	1	1	-	1
1.024	1	1	1	1	1	1	1	-	1
1.025	7	2	7	3	1	3	1	-	1
1.026	7	1	4	3	1	1	2	-	1
1.027	3	1	2	1	1	1	1	-	1
1.032	4	1	7	1	2	1	3	-	1
1.033	2	1	1	1	1	1	1	-	1
1.034	1	1	2	2	1	2	1	-	1
1.035	5	1	4	1	1	1	1	-	1
1.041	2	1	1	1	1	1	1	-	1
1.042	1	2	5	3	1	1	2	-	1
1.048	7	3	7	3	2	2	2	-	3
1.052	2	1	3	2	2	2	3	-	1
1.053	2	1	3	1	1	1	1	-	1
1.054	2	1	1	1	1	1	1	-	1
1.055	2	1	1	2	1	1	1	-	1
1.056	2	1	2	2	1	1	1	-	1
1.057	2	1	1	1	1	1	1	-	1
1.058	2	1	2	1	1	1	1	-	1
1.059	2	2	2	2	1	2	1	-	1
1.060	1	1	1	2	1	1	1	1	1
1.061	2	1	2	2	1	1	1	1	1
1.062	4	1	1	3	1	1	1	1	1
1.063	1	1	1	1	1	1	1	1	1
1.064	1	1	1	1	1	1	1	1	1
1.065	1	1	1	2	1	1	1	1	1

1.066	1	1	1	1	1	1	1	1	1
1.067	1	1	1	2	1	1	1	1	1
1.068	1	1	1	1	1	1	1	1	1
1.069	1	1	1	1	1	1	1	1	1
1.070	2	1	2	2	1	1	1	1	1
1.071	2	1	1	2	1	1	1	1	1
1.072	1	1	1	3	1	1	1	1	1
1.073	3	1	1	2	1	1	1	1	1
1.074	1	1	1	2	1	1	1	1	1
12.002	3	4	6	2	1	1	3	1	1
5.002	4	2	6	1	1	1	1	1	1
11.003	2	1	1	2	1	1	1	1	1
11.004	4	1	1	2	1	2	1	1	1
11.005	1	1	1	2	1	1	1	1	1
11.006	3	2	3	2	1	2	1	1	1
5.003	4	4	4	1	1	1	1	1	1
1.107	1	1	1	1	1	2	1	1	1
5.004	3	2	2	1	1	1	1	1	1
5.005	2	2	4	2	1	1	1	1	1
1.075	3	1	3	2	1	3	2	1	1
1.077	1	1	1	1	1	1	1	1	1
1.078	1	1	1	1	1	1	1	1	1
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1.087	3	1	2	2	1	4	1	1	1
1.088	1	1	1	2	1	1	1	1	1
1.089	1	1	1	2	1	1	1	1	1
1.090	5	1	3	2	1	1	1	1	1
1.091	1	1	1	2	1	1	1	1	1
1.092	1	1	1	2	2	1	1	1	1

The same results are obtained when the compounds of formula I are formulated in accordance with Examples F2 and F4 to F8 according to WO 97/34485.

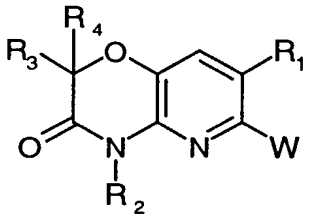
The compounds of formula I according to the invention can also be used for weed control in admixture with known herbicides as co-herbicides, for example in the form of ready-prepared formulations or in the form of a 'tank-mix'. Suitable mixing partners for the compounds of formula I include, for example, the following co-herbicides: compound of formula I + acetochlor; compound of formula I + acifluorfen; compound of formula I + aclonifen; compound of formula I + alachlor; compound of formula I + ametryn; compound of formula I + aminotriazole; compound of formula I + amidosulfuron; compound of formula I + asulam; compound of formula I + atrazine; compound of formula I + BAY FOE 5043; compound of formula I + benazolin; compound of formula I + bensulfuron; compound of

formula I + bentazone; compound of formula I + bifenox; compound of formula I + bispyribac-sodium; compound of formula I + bialaphos; compound of formula I + bromacil; compound of formula I + bromoxynil; compound of formula I + bromophenoxim; compound of formula I + butachlor; compound of formula I + butylate; compound of formula I + cafenstrole; compound of formula I + carbetamide; compound of formula I + chloridazone; compound of formula I + chlorimuron-ethyl; compound of formula I + chlorbromuron; compound of formula I + chlorsulfuron; compound of formula I + chlortoluron; compound of formula I + cinosulfuron; compound of formula I + clethodim; compound of formula I + clodinafop; compound of formula I + clomazone; compound of formula I + clopyralid; compound of formula I + cloransulam; compound of formula I + cyanazine; compound of formula I + cyhalofop; compound of formula I + dalapon; compound of formula I + 2,4-D; compound of formula I + 2,4-DB; compound of formula I + desmetryn; compound of formula I + desmedipham; compound of formula I + dicamba; compound of formula I + diclofop; compound of formula I + difenzoquat metilsulfate; compound of formula I + diflufenican; compound of formula I + dimefuron; compound of formula I + dimepiperate; compound of formula I + dimethachlor; compound of formula I + dimethametryn; compound of formula I + dimethenamid; compound of formula I + S-dimethenamid; compound of formula I + dinitramine; compound of formula I + dinoterb; compound of formula I + dipropetryn; compound of formula I + diuron; compound of formula I + diquat; compound of formula I + DSMA; compound of formula I + EPTC; compound of formula I + esprocarb; compound of formula I + ethalfluralin; compound of formula I + ethametsulfuron; compound of formula I + ethephon; compound of formula I + ethofumesate; compound of formula I + ethoxysulfuron; compound of formula I + fenclorim; compound of formula I + flamprop; compound of formula I + fluazasulfuron; compound of formula I + fluazifop; compound of formula I + flumetralin; compound of formula I + flumetsulam; compound of formula I + fluometuron; compound of formula I + flurochloridone; compound of formula I + fluoxaprop; compound of formula I + fluroxypyr; compound of formula I + fluthiacet-methyl; compound of formula I + fluxofenim; compound of formula I + fomesafen; compound of formula I + glufosinate; compound of formula I + glyphosate; compound of formula I + halosulfuron; compound of formula I + haloxyfop; compound of formula I + hexazinone; compound of formula I + imazamethabenz; compound of formula I + imazapyr; compound of formula I + imazaquin; compound of formula I + imazethapyr; compound of formula I + imazosulfuron; compound of formula I + ioxynil; compound of formula I + isoproturon; compound of formula I + isoxaben; compound of formula I + isoxaflutole; compound of formula I + karbutylate; compound of formula I + lactofen; compound of formula I + lenacil; compound of formula I + linuron; compound of formula I + MCPP; compound of formula I + metamitron;

compound of formula I + metazachlor; compound of formula I + methabenzthiazuron; compound of formula I + methazole; compound of formula I + metobromuron; compound of formula I + metolachlor; compound of formula I + S-metolachlor; compound of formula I + metosulam; compound of formula I + metribuzin; compound of formula I + metsulfuron-methyl; compound of formula I + molinate; compound of formula I + MCPA; compound of formula I + MSMA; compound of formula I + napropamide; compound of formula I + NDA-402989; compound of formula I + nefenacet; compound of formula I + nicosulfuron; compound of formula I + norflurazon; compound of formula I + oryzalin; compound of formula I + oxadiazon; compound of formula I + oxasulfuron; compound of formula I + oxyfluorfen; compound of formula I + paraquat; compound of formula I + pendimethalin; compound of formula I + phenmedipham; compound of formula I + phenoxaprop-P-ethyl (R); compound of formula I + picloram; compound of formula I + pretilachlor; compound of formula I + primisulfuron; compound of formula I + prometon; compound of formula I + prometryn; compound of formula I + propachlor; compound of formula I + propanil; compound of formula I + propazine; compound of formula I + propaquizafop; compound of formula I + propyzamide; compound of formula I + prosulfuron; compound of formula I + pyrazolynate; compound of formula I + pyrazosulfuron-ethyl; compound of formula I + pyrazoxyphen; compound of formula I + pyridate; compound of formula I + pyriminobac-methyl; compound of formula I + pyrithiobac-sodium; compound of formula I + quinclorac; compound of formula I + quizalofop; compound of formula I + rimsulfuron; compound of formula I + sequestrene; compound of formula I + sethoxydim; compound of formula I + simetryn; compound of formula I + simazine; compound of formula I + sulcotrione; compound of formula I + sulfosate; compound of formula I + sulfosulfuron-methyl; compound of formula I + tebutam; compound of formula I + tebuthiuron; compound of formula I + terbacil; compound of formula I + terbumeton; compound of formula I + terbuthylazine; compound of formula I + terbutryn; compound of formula I + thiazafluron; compound of formula I + thiazopyr; compound of formula I + thifensulfuron-methyl; compound of formula I + thiobencarb; compound of formula I + tralkoxydim; compound of formula I + triallate; compound of formula I + triasulfuron; compound of formula I + trifluralin; compound of formula I + tribenuron-methyl; compound of formula I + triclopyr; compound of formula I + triflusulfuron; and compound of formula I + trinexapac-ethyl, and esters and salts of those mixing partners for the compound of formula I that are mentioned e.g. in The Pesticide Manual, Eleventh Edition, 1997, BCPC.

What is claimed is:

1. A compound of formula I



(I)

wherein

R_1 is hydrogen, methyl or halogen;

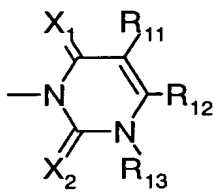
R_2 is hydrogen, C_1-C_{12}alkyl, C_1-C_{12}haloalkyl, C_2-C_{12}alkenyl, C_2-C_{12}alkynyl, C_2-C_8alkynyl-C_2-C_4alkenyl, C_3-C_{12}allenyl, C_2-C_{12}haloalkenyl, C_2-C_{12}haloalkynyl, C_3-C_6cycloalkyl, C_3-C_6cycloalkyl-C_1-C_4alkyl, C_3-C_6halocycloalkyl-C_1-C_4alkyl, tri(C_1-C_4alkyl)silyl-C_1-C_4alkyl, tri(C_1-C_4alkyl)silyl-C_2-C_4alkenyl, cyano-C_1-C_{12}alkyl, C_1-C_6alkoxy-C_1-C_4alkyl, C_1-C_4alkoxy-C_1- or -C_2-alkoxy-C_1- or -C_2-alkyl, di(C_1-C_4alkoxy)-C_1- or -C_2-alkyl, ethylenedioxy-C_1- or -C_2-alkyl, C_2-C_6alkenyloxy-C_1-C_4alkyl, C_2-C_6haloalkenyloxy-C_1-C_4alkyl, C_2-C_6alkynyloxy-C_1-C_4alkyl, C_3-C_6haloalkynyloxy-C_1-C_4alkyl, C_1-C_6alkylthio-C_1-C_4alkyl, C_1-C_6alkylsulfinyl-C_1-C_4alkyl, C_1-C_6alkylsulfonyl-C_1-C_4alkyl, hydroxy-C_1-C_{12}alkyl, C_1-C_6alkylcarbonyl-C_1-C_4alkyl, C_1-C_6haloalkylcarbonyl-C_1-C_4alkyl, C_1-C_6alkoxycarbonyl-C_1-C_4alkyl, C_1-C_6alkoxy-C_1- or -C_2-alkoxycarbonyl-C_1-C_4alkyl, C_1-C_6alkoxycarbonyl-C_1-C_4haloalkyl, C_3-C_6cycloalkylcarbonyl-C_1-C_4alkyl or benzoyl-C_1-C_4alkyl wherein the benzoyl group may be substituted by halogen, C_1-C_3alkyl, C_1-C_3haloalkyl, C_1-C_3alkoxy or by C_1-C_3haloalkoxy, or is C_3-C_6alkenyloxycarbonyl-C_1-C_4alkyl, C_3-C_6alkynyloxycarbonyl-C_1-C_4alkyl, C_1-C_6alkylcarbonyloxy-C_1-C_4alkyl, C_2-C_6alkenylcarbonyloxy-C_1-C_4alkyl, C_3-C_6cycloalkylcarbonyloxy-C_1-C_4alkyl, benzoyloxy-C_1-C_4alkyl, C_1-C_6alkoxycarbonyloxy-C_1-C_4alkyl, carbamoyl-C_1-C_4alkyl, C_1-C_6alkylaminocarbonyl-C_1-C_4alkyl, or phenyl- or heterocyclyl-substituted C_1-C_4alkyl, wherein the phenyl and heterocyclyl groups may be substituted by halogen, C_1-C_6alkyl, C_1-C_6alkoxy, C_1-C_6haloalkyl, C_1-C_6haloalkoxy, C_2-C_6alkenyl, C_2-C_6alkynyl, C_2-C_6haloalkenyl, C_2-C_6haloalkynyl, C_3-C_6cycloalkyl-C_1-C_4alkyl, C_3-C_6halocycloalkyl-C_1-C_4alkyl, cyano-C_1-C_4alkyl, C_1-C_6alkoxy-C_1-C_4alkyl, C_1-C_6alkylthio-C_1-C_4alkyl, C_1-C_6alkylsulfinyl-C_1-C_4alkyl, C_1-C_6alkylsulfonyl-C_1-C_4alkyl, hydroxy-C_1-C_4alkyl, C_1-C_6alkylcarbonyl-C_1-C_4alkyl, C_1-C_6alkoxycarbonyl, C_1-C_6alkoxy-carbonyl-C_1-C_4alkyl, C_1-C_6alkoxycarbonyl-C_1-C_4haloalkyl, C_1-C_6alkoxycarbonyl-C_1-C_4alkoxy, C_1-C_6alkylcarbonyloxy-C_1-C_4alkyl, C_1-C_6alkoxycarbonyloxy-C_1-C_4alkyl, C_1-C_4alkoxy-C_1-C_2alkoxy-C_1-C_2alkyl, C_1-C_4alkylaminocarbonyl, C_1-C_6alkylaminocarbonyl-C_1-C_4alkoxy, phenyl, phenoxy or by benzyloxy, wherein the phenyl ring of the last three definitions may

be substituted by halogen, methyl, trifluoromethyl, methylsulfonyl, methoxy, ethoxy or by cyano; or is phenyl-substituted C_2-C_4alkenyl or C_2-C_4alkynyl, wherein the phenyl group may be substituted by halogen, methyl, trifluoromethyl, methylthio, methylsulfinyl, methylsulfonyl, methoxy, ethoxy, cyano or by nitro;

R_3 is hydrogen, C_1-C_{12}alkyl, C_1-C_{12}haloalkyl, C_1-C_6alkoxycarbonyl, or phenyl which is unsubstituted or substituted by halogen, methyl, trifluoromethyl, methylthio, methylsulfinyl, methylsulfonyl, methoxy, ethoxy, cyano or by nitro;

R_4 is hydrogen or C_1-C_6alkyl;

W is a group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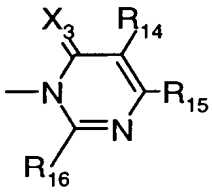
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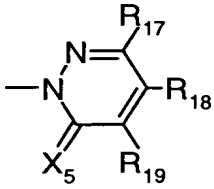
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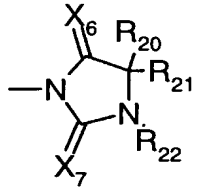
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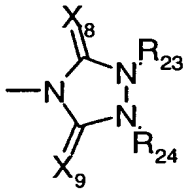
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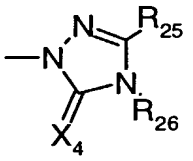
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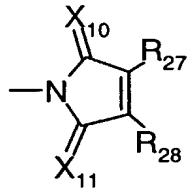
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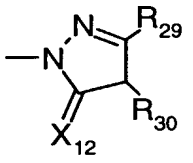
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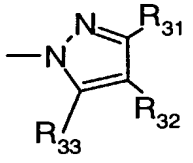
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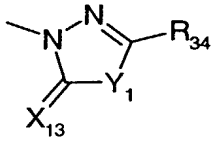
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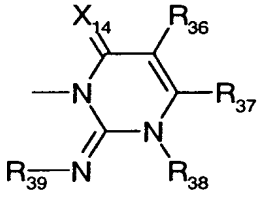
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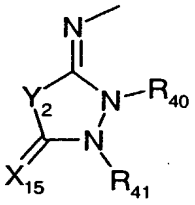
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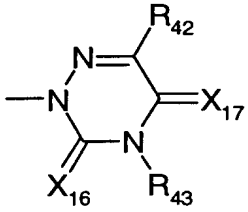
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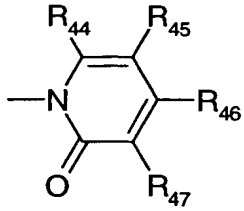
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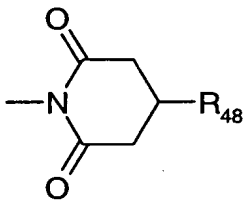
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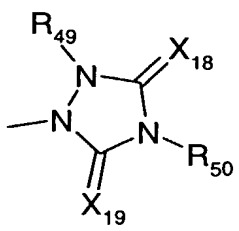
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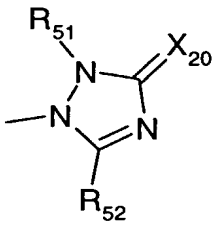
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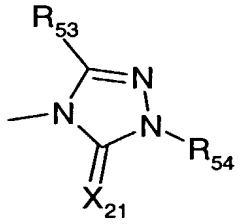
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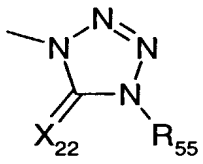
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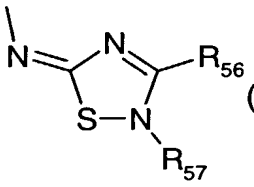
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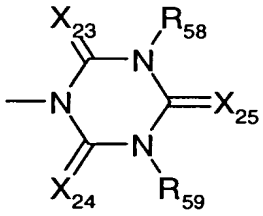
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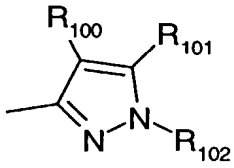
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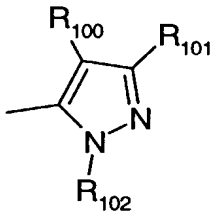
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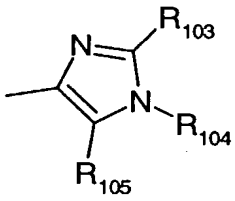
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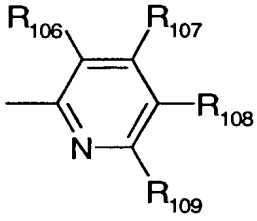
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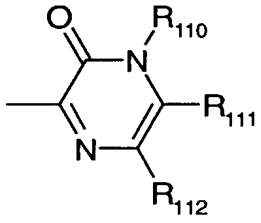
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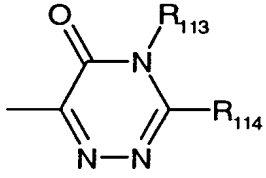
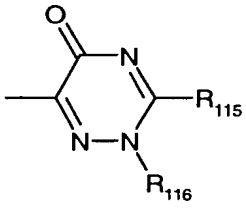

(W105),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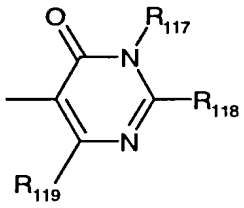
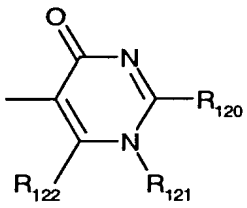
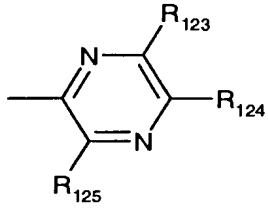

(W107),

(W108) or


(W109);

R_{11} is hydrogen, C_1-C_3alkyl, halogen, C_1-C_3haloalkyl or cyano;

R_{12} is C_1-C_3alkyl, C_1-C_3haloalkyl, C_1-C_3alkyl-$S(O)_{n1}$-, C_1-C_3haloalkyl-$S(O)_{n1}$- or cyano; and

R_{13} is hydrogen, C_1-C_3alkyl, C_1-C_3haloalkyl, allyl, propargyl or amino; or

R_{12} and R_{11} or R_{12} and R_{13} together form a C_3- or C_4-alkylene bridge which may be substituted by halogen, C_1-C_3haloalkyl or by cyano;

R_{14} is hydrogen, C_1-C_3alkyl, halogen, C_1-C_3haloalkyl or cyano; and

R_{15} is C_1-C_3alkyl, C_1-C_3haloalkyl, C_1-C_3alkyl-$S(O)_{n2}$-, C_1-C_3haloalkyl-$S(O)_{n2}$- or cyano; or

R_{15} and R_{14} together form a C_3- or C_4-alkylene bridge which may be substituted by halogen, C_1-C_3haloalkyl or by cyano;

R_{16} is hydrogen, C_1-C_3alkyl, halogen, C_1-C_3haloalkyl, C_1-C_3alkoxy, C_1-C_3haloalkoxy, hydroxy, mercapto, C_1-C_3alkylthio, allylthio, propargylthio, C_1-C_3alkylsulfinyl, C_1-C_3alkylsulfonyl, amino, C_1-C_3alkylamino, di(C_1-C_3alkyl)amino, allylamino, propargylamino or cyano;

n_1 and n_2 are 0, 1 or 2;

R_{17} is hydrogen, C_1-C_3alkyl, halogen or cyano; and

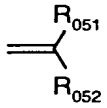
R_{18} is C_1-C_3alkyl, halogen, C_1-C_3haloalkyl, C_1-C_3alkylthio, C_1-C_3alkylsulfinyl, C_1-C_3alkylsulfonyl or cyano; or

R_{18} and R_{17} together form a C_3- or C_4-alkylene or C_3- or C_4-alkenylene bridge, both of which may be substituted by halogen, C_1-C_3alkyl or by C_1-C_3haloalkyl;

R_{19} is hydrogen, halogen, C_1-C_3alkyl, carboxyl, C_1-C_3alkoxycarbonyl or amino; or

R_{19} and R_{18} together form a C_3- or C_4-alkylene or C_3- or C_4-alkenylene bridge, both of which may be substituted by halogen, C_1-C_3alkyl or by C_1-C_3haloalkyl;

R_{20} and R_{21} are each independently of the other hydrogen or C_1-C_4alkyl; or

R_{20} and R_{21} together are a group  ;

R_{051} and R_{052} are each independently of the other hydrogen or C_1-C_4alkyl; or

R_{051} and R_{052} together form a C_4- or C_5-alkylene bridge;

R_{052} and R_{22} together form a C_3alkylene bridge;

R_{22} is hydrogen or C_1-C_3alkyl; or

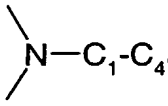
R_{22} and R_{20} or R_{22} and R_{21} together form a C_3-C_5alkylene bridge which may be interrupted by oxygen, sulfur, -S(O)-, -$S(O)_2$- or by –C(O)- and/or substituted by halogen, C_1-C_4alkyl, C_1-C_3haloalkyl, C_2-C_4alkenyl, C_1-C_3alkoxycarbonyl, C_1-C_3alkylcarbonyloxy, C_1-C_3alkylsulfonyloxy or by hydroxy;

R_{23} and R_{24} are each independently of the other hydrogen, C_1-C_3alkyl, C_1-C_3haloalkyl or propargyl; or

R_{23} and R_{24} together form a C_3-C_5alkylene bridge which may be interrupted by oxygen, sulfur, -S(O)-, -$S(O)_2$- or by -C(O)- and/or substituted by halogen, C_1-C_4alkyl, hydroxy, C_1-C_4alkoxy or by C_1-C_4alkoxy-C_1-C_4alkoxy;

R_{25} is hydrogen, halogen, C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4alkoxy, C_1-C_4haloalkoxy, C_1-C_4alkylthio, C_1-C_4haloalkylthio, C_1-C_4alkylsulfinyl, C_1-C_4haloalkylsulfinyl, C_1-C_4alkylsulfonyl, C_1-C_4haloalkylsulfonyl, hydroxy or cyano; and

R_{26} is hydrogen, C_1-C_4alkyl or C_1-C_4haloalkyl; or

R_{26} and R_{25} together form a C_3-C_5alkylene bridge which may be interrupted by oxygen, sulfur, -S(O)-, -$S(O)_2$-,  or by –C(O)- and/or substituted by halogen, C_1-C_4alkyl, C_1-C_3haloalkyl, C_2-C_4alkenyl, C_1-C_3alkoxycarbonyl, C_1-C_3alkylcarbonyloxy, C_1-C_3alkylsulfonyloxy or by hydroxy;

R_{27} and R_{28} are each independently of the other hydrogen or C_1-C_4alkyl; or

R_{27} and R_{28} together form a C_3-C_5alkylene bridge which may be substituted by halogen or by C_1-C_4alkyl and/or interrupted by oxygen, sulfur, -S(O)-, -$S(O)_2$- or by -C(O)- or form a C_4alkenylene bridge which is unsubstituted or substituted by C_1-C_4alkyl;

R_{29} and R_{30} are each independently of the other hydrogen, C_1-C_4alkyl or C_1-C_4haloalkyl; or

R_{29} and R_{30} together form a C_3-C_5alkylene bridge which may be substituted by halogen or by C_1-C_4alkyl and/or interrupted by oxygen, sulfur, -S(O)-, -$S(O)_2$- or by -C(O)-;

R_{31} is hydrogen, C_1-C_4alkyl or C_1-C_4haloalkyl; and

R_{32} is hydrogen, C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4alkylthio, C_1-C_4alkylsulfinyl, C_1-C_4alkylsulfonyl, cyano or nitro; or

R_{31} and R_{32} together form a C_3-C_5alkylene bridge which may be substituted by halogen or by C_1-C_4alkyl and/or interrupted by oxygen, sulfur, -S(O)-, -$S(O)_2$- or by -C(O)- or form a C_4alkenylene bridge which is unsubstituted or substituted by C_1-C_4alkyl;

R_{33} is hydrogen, C_1-C_3alkyl, halogen, C_1-C_3haloalkyl, hydroxy, C_1-C_3alkoxy, C_1-C_3haloalkoxy, mercapto, C_1-C_3alkylthio, C_1-C_3alkylsulfinyl, C_1-C_3alkylsulfonyl, amino, C_1-C_3alkylamino, C_1-C_3alkylcarbonylamino, C_1-C_3haloalkylcarbonylamino or cyano;

R_{34} is C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4alkoxy or C_1-C_4alkylthio;

R_{36} is hydrogen, C_1-C_3alkyl, halogen, C_1-C_3haloalkyl or cyano; and

R_{37} is C_1-C_3alkyl, C_1-C_3haloalkyl, C_1-C_3alkyl-$S(O)_{n1}$-, C_1-C_3haloalkyl-$S(O)_{n1}$- or cyano; or

R_{37} and R_{36} together form a C_3- or C_4-alkenylene bridge which may be substituted by halogen, C_1-C_3alkyl, C_1-C_3haloalkyl or by cyano;

R_{38} is C_1-C_3alkyl; and

R_{39} is hydrogen or C_1-C_3alkyl; or

R_{39} and R_{38} together form a C_2- or C_3-alkylene or C_2- or C_3-alkenylene bridge which is unsubstituted or substituted by C_1-C_4alkyl or form an -NH-CH_2-, -N=CH- or -N=N- bridge;

R_{40} and R_{41} are each independently of the other C_1-C_3alkyl or C_1-C_3haloalkyl; or

R_{41} and R_{40} together form a C_3-C_5alkylene bridge which is unsubstituted or substituted by halogen or by C_1-C_4alkyl;

R_{42} is hydrogen, C_1-C_3alkyl, C_1-C_3haloalkyl, cyano or carboxyl;

R_{43} is hydrogen, C_1-C_3alkyl, C_1-C_3haloalkyl, allyl or propargyl;

R_{44} is hydrogen, C_1-C_3alkyl, halogen, C_1-C_3haloalkyl, hydroxy, mercapto, amino, C_1-C_3alkoxy, C_1-C_3alkylthio or di(C_1-C_4alkyl)amino;

R_{45} is hydrogen, C_1-C_3alkyl, halogen or cyano;

R_{46} is C_1-C_3alkyl, C_1-C_3haloalkyl or cyano;

R_{47} is hydrogen, C_1-C_3alkyl or halogen;

R_{48} is C_1-C_3alkyl or C_1-C_3haloalkyl;

R_{49}, R_{50} and R_{51} are each independently of the others hydrogen, C_1-C_4alkyl, propargyl or C_1-C_4haloalkyl;

R_{52} is C_1-C_3alkyl, halogen, C_1-C_3haloalkyl, C_1-C_3alkoxy, C_1-C_3haloalkoxy, C_1-C_3alkylthio, C_1-C_3alkylsulfinyl, C_1-C_3alkylsulfonyl, amino or C_1-C_3alkylamino;

R_{53} is C_1-C_3alkyl or C_1-C_3haloalkyl;

R_{54} is C_1-C_3alkyl;

R_{55} is hydrogen, C_1-C_3alkyl, propargyl or C_1-C_3haloalkyl;

R_{56} is C_1-C_3alkyl, C_1-C_3haloalkyl, C_1-C_3alkylthio, C_1-C_3alkylsulfinyl or C_1-C_3alkylsulfonyl; and

R_{57} is C_1-C_3alkyl or C_1-C_3haloalkyl; or

R_{57} and R_{56} together form a C_2-C_4alkylene or C_2-C_4alkenylene bridge which both are unsubstituted or substituted by halogen or by C_1-C_4alkyl;

R_{58} is hydrogen, C_1-C_3alkyl, C_1-C_3haloalkyl or amino;

R_{59} is hydrogen, C_1-C_3alkyl or C_1-C_3haloalkyl;

R_{100} is hydrogen, halogen, nitro, amino, cyano, C_1-C_3alkyl, C_2- or C_3-alkenyl or C_2- or C_3-alkynyl;

R_{101} is hydrogen, halogen, nitro, amino, cyano, hydroxy, mercapto, C_1-C_3alkyl, C_1-C_3haloalkyl, C_2- or C_3-alkenyl, C_2- or C_3-alkynyl, C_1-C_3alkoxy, C_1-C_3haloalkoxy, C_1-C_3alkylthio, C_1-C_3alkylsulfinyl, C_1-C_3alkylsulfonyl, C_1-C_3haloalkylthio, C_1-C_3haloalkylsulfinyl, C_1-C_3haloalkylsulfonyl, $FS(O)_2$-, $ClS(O)_2$-, C_1-C_6alkylsulfonyloxy, C_1-C_6haloalkylsulfonyloxy, C_1-C_3alkylcarbonyl, HC(O)-, HOC(O)-, ClC(O)-, FC(O)-, C_1-C_3alkoxycarbonyl, $H_2NC(O)$- or $H_2NC(S)$-; and

R_{102} is hydrogen, C_1-C_6alkyl, C_1-C_6alkyl substituted by cyano, HO-, HOC(O)-, C_1-C_3alkoxycarbonyl or by HC(O)-, or is C_3-C_6alkenyl, C_3-C_6alkynyl, C_3-C_6cycloalkyl, C_1-C_6haloalkyl or C_1-C_3alkylsulfonyl; or

when W is a group W_{100},

R_{102} and R_{101} together form a C_3-C_5alkylene bridge which may be interrupted by oxygen, sulfur, -S(O)-, -$S(O)_2$- or by -C(O)- and/or substituted by hydroxy or by halogen;

R_{103} is hydrogen, halogen, nitro, amino, cyano, hydroxy, mercapto, C_1-C_3alkyl, C_1-C_3haloalkyl, C_2- or C_3-alkenyl, C_2- or C_3-alkynyl, C_1-C_3alkoxy, C_1-C_3haloalkoxy, C_1-C_3alkylthio, C_1-C_3alkylsulfinyl, C_1-C_3alkylsulfonyl, C_1-C_3haloalkylthio, C_1-C_3haloalkylsulfinyl, C_1-C_3haloalkylsulfonyl, $FS(O)_2$-, $ClS(O)_2$-, C_1-C_6alkylsulfonyloxy, C_1-C_6haloalkylsulfonyloxy, C_1-C_3alkylcarbonyl, HC(O)-, HOC(O)-, ClC(O)-, FC(O)-, C_1-C_3alkoxycarbonyl, $H_2NC(O)$- or $H_2NC(S)$-;

R_{104} is hydrogen, C_1-C_6alkyl, C_1-C_6alkyl substituted by cyano, HO-, HOC(O)-, C_1-C_3alkoxy-carbonyl or by HC(O)-, or is C_3-C_6alkenyl, C_3-C_6alkynyl, C_3-C_6cycloalkyl, C_1-C_6haloalkyl or C_1-C_3alkylsulfonyl; and

R_{105} is hydrogen, halogen, nitro, amino, cyano, C_1-C_3alkyl, C_2- or C_3-alkenyl or C_2- or C_3-alkynyl; or

R_{104} and R_{103} together form a C_3-C_5alkylene bridge or a C_4alkenylene bridge which both may be interrupted by oxygen, sulfur, -S(O)-, -$S(O)_2$- or by -C(O)- and/or substituted by hydroxy or by halogen;

R_{106} is hydrogen, halogen, amino, nitro, hydroxy, C_1-C_3alkyl or C_1-C_3alkoxy;

R_{107} is hydrogen, halogen, amino, hydroxy, C_1-C_3alkyl, C_1-C_3haloalkyl, HC(O)-, HOC(O)-, hydroxy-C_1-C_3alkyl, C_1-C_3alkoxy or C_1-C_3haloalkoxy; and

R_{108} is hydrogen, halogen, nitro, amino, cyano, HC(O)-, HOC(O)-, $H_2NC(O)$-, $H_2NC(S)$-, hydroxy, mercapto, C_1-C_3alkyl, C_1-C_3haloalkyl, C_2- or C_3-alkenyl, C_1-C_3alkoxy, C_1-C_3haloalkoxy, C_1-C_3alkylcarbonyl, C_1-C_3alkoxycarbonyl, C_1-C_3alkylthio, C_1-C_3haloalkylthio, C_1-C_3alkylsulfinyl, C_1-C_3haloalkylsulfinyl, C_1-C_3alkylsulfonyl, C_1-C_3haloalkylsulfonyl, C_1-C_3alkylsulfonyloxy or C_1-C_3haloalkylsulfonyloxy; or

R_{108} and R_{107} together form a C_3-C_5alkylene bridge which may be interrupted by oxygen, sulfur, -S(O)-, -$S(O)_2$- or by -C(O)- and/or substituted by hydroxy or by halogen;

R_{109} is hydrogen, halogen, amino, hydroxy, C_1-C_3alkyl, C_1-C_3haloalkyl, HC(O)-, HOC(O)-, hydroxy-C_1-C_3alkyl, C_1-C_3alkoxy or C_1-C_3haloalkoxy; or

R_{109} and R_{108} together form a C_3-C_5alkylene bridge which may be interrupted by oxygen, sulfur, -S(O)-, -$S(O)_2$- or by -C(O)- and/or substituted by hydroxy or by halogen;

R_{110} is hydrogen, C_1-C_3alkyl, C_1-C_3haloalkyl, C_3-C_4alkenyl or C_3-C_4alkynyl;

R_{111} is hydrogen, halogen, nitro, amino, cyano, HC(O)-, HOC(O)-, $H_2NC(O)$-, $H_2NC(S)$-, hydroxy, mercapto, C_1-C_3alkyl, C_1-C_3haloalkyl, C_2- or C_3-alkenyl, C_1-C_3alkoxy, C_1-C_3haloalkoxy, C_1-C_3alkylcarbonyl, C_1-C_3alkoxycarbonyl, C_1-C_3alkylthio, C_1-C_3haloalkylthio, C_1-C_3alkylsulfinyl, C_1-C_3haloalkylsulfinyl, C_1-C_3alkylsulfonyl, C_1-C_3haloalkylsulfonyl, C_1-C_3alkylsulfonyloxy or C_1-C_3haloalkylsulfonyloxy; and

R_{112} is hydrogen, halogen, amino, hydroxy, C_1-C_3alkyl, C_1-C_3haloalkyl, HC(O)-, HOC(O)-, hydroxy-C_1-C_3alkyl, C_1-C_3alkoxy or C_1-C_3haloalkoxy; or

R_{111} and R_{110} together form a C_3-C_5alkylene bridge which may be interrupted by oxygen, sulfur, -S(O)-, $-S(O)_2$- or by -C(O)- and/or substituted by hydroxy or by halogen, wherein the C_3-C_5alkylene bridge is bonded to the N atom of the pyrazinone *via* a CH_2 group; or

R_{112} and R_{111} together form a C_3-C_5alkylene bridge which may be interrupted by oxygen, sulfur, -S(O)-, $-S(O)_2$- or by -C(O)- and/or substituted by hydroxy or by halogen;

R_{113} is hydrogen, C_1-C_3alkyl, C_1-C_3haloalkyl, C_3-C_4alkenyl or C_3-C_4alkynyl; and

R_{114} is hydrogen, halogen, nitro, amino, cyano, HC(O)-, HOC(O)-, $H_2NC(O)$-, $H_2NC(S)$-, hydroxy, mercapto, C_1-C_3alkyl, C_1-C_3haloalkyl, C_2- or C_3-alkenyl, C_1-C_3alkoxy, C_1-C_3haloalkoxy, C_1-C_3alkylcarbonyl, C_1-C_3alkoxycarbonyl, C_1-C_3alkylthio, C_1-C_3haloalkylthio, C_1-C_3alkylsulfinyl, C_1-C_3haloalkylsulfinyl, C_1-C_3alkylsulfonyl, C_1-C_3haloalkylsulfonyl, C_1-C_3alkylsulfonyloxy, C_1-C_3haloalkylsulfonyloxy, C_1-C_3alkylamino or di(C_1-C_3alkyl)amino; or

R_{114} and R_{113} together form a C_3-C_5alkylene bridge which may be interrupted by oxygen, sulfur, -S(O)-, $-S(O)_2$- or by -C(O)- and/or substituted by hydroxy or by halogen, wherein the C_3-C_5alkylene bridge is bonded to the N atom of the triazinone *via* a CH_2 group;

R_{115} is hydrogen, halogen, nitro, amino, cyano, HC(O)-, HOC(O)-, $H_2NC(O)$-, $H_2NC(S)$-, hydroxy, mercapto, C_1-C_3alkyl, C_1-C_3haloalkyl, C_2- or C_3-alkenyl, C_1-C_3alkoxy, C_1-C_3haloalkoxy, C_1-C_3alkylcarbonyl, C_1-C_3alkoxycarbonyl, C_1-C_3alkylthio, C_1-C_3haloalkylthio, C_1-C_3alkylsulfinyl, C_1-C_3haloalkylsulfinyl, C_1-C_3alkylsulfonyl, C_1-C_3haloalkylsulfonyl, C_1-C_3alkylsulfonyloxy or C_1-C_3haloalkylsulfonyloxy; and

R_{116} is hydrogen, C_1-C_3alkyl, C_1-C_3haloalkyl, C_3-C_4alkenyl or C_3-C_4alkynyl; or

R_{116} and R_{115} together form a C_3-C_5alkylene bridge which may be interrupted by oxygen, sulfur, -S(O)-, $-S(O)_2$- or by -C(O)- and/or substituted by hydroxy or by halogen, wherein the C_3-C_5alkylene bridge is bonded to the N atom of the triazinone *via* a CH_2 group;

R_{117} is hydrogen, C_1-C_3alkyl, C_1-C_3haloalkyl, C_3-C_4alkenyl or C_3-C_4alkynyl;

R_{118} is hydrogen, halogen, nitro, amino, cyano, HC(O)-, HOC(O)-, $H_2NC(O)$-, $H_2NC(S)$-, hydroxy, mercapto, C_1-C_3alkyl, C_1-C_3haloalkyl, C_2- or C_3-alkenyl, C_1-C_3alkoxy, C_1-C_3haloalkoxy, C_1-C_3alkylcarbonyl, C_1-C_3alkoxycarbonyl, C_1-C_3alkylthio, C_1-C_3haloalkylthio,

C_1-C_3alkylsulfinyl, C_1-C_3haloalkylsulfinyl, C_1-C_3alkylsulfonyl, C_1-C_3haloalkylsulfonyl, C_1-C_3alkylsulfonyloxy or C_1-C_3haloalkylsulfonyloxy; and

R_{119} is hydrogen, halogen, amino, nitro, hydroxy, C_1-C_3alkyl or C_1-C_3alkoxy; or

R_{118} and R_{117} together form a C_3-C_5alkylene bridge which may be interrupted by oxygen, sulfur, -S(O)-, -$S(O)_2$- or by -C(O)- and/or substituted by hydroxy or by halogen, wherein the C_3-C_5alkylene bridge is bonded to the N atom of the pyrimidinone *via* a CH_2 group;

R_{120} is hydrogen, halogen, nitro, amino, cyano, HC(O)-, HOC(O)-, $H_2NC(O)$-, $H_2NC(S)$-, hydroxy, mercapto, C_1-C_3alkyl, C_1-C_3haloalkyl, C_2- or C_3-alkenyl, C_1-C_3alkoxy, C_1-C_3haloalkoxy, C_1-C_3alkylcarbonyl, C_1-C_3alkoxycarbonyl, C_1-C_3alkylthio, C_1-C_3haloalkylthio, C_1-C_3alkylsulfinyl, C_1-C_3haloalkylsulfinyl, C_1-C_3alkylsulfonyl, C_1-C_3haloalkylsulfonyl, C_1-C_3alkylsulfonyloxy or C_1-C_3haloalkylsulfonyloxy;

R_{121} is hydrogen, C_1-C_3alkyl, C_1-C_3haloalkyl, C_3- or C_4-alkenyl or C_3- or C_4-alkynyl; and

R_{122} is hydrogen, halogen, amino, nitro, hydroxy, C_1-C_3alkyl or C_1-C_3alkoxy; or

R_{121} and R_{120} together form a C_3-C_5alkylene bridge which may be interrupted by oxygen, sulfur, -S(O)-, -$S(O)_2$- or by -C(O)- and/or substituted by hydroxy or by halogen, wherein the C_3-C_5alkylene bridge is bonded to the N atom of the pyrimidinone *via* a CH_2 group;

R_{123} is hydrogen, C_1-C_3alkyl, halogen or C_1-C_3haloalkyl;

R_{124} is hydrogen, halogen, nitro, amino, cyano, HC(O)-, HOC(O)-, $H_2NC(O)$-, $H_2NC(S)$-, hydroxy, mercapto, C_1-C_3alkyl, C_1-C_3haloalkyl, C_2- or C_3-alkenyl, C_1-C_3alkoxy, C_1-C_3haloalkoxy, C_1-C_3alkylcarbonyl, C_1-C_3alkoxycarbonyl, C_1-C_3alkylthio, C_1-C_3haloalkylthio, C_1-C_3alkylsulfinyl, C_1-C_3haloalkylsulfinyl, C_1-C_3alkylsulfonyl, C_1-C_3haloalkylsulfonyl, C_1-C_3alkylsulfonyloxy or C_1-C_3haloalkylsulfonyloxy; and

R_{125} is hydrogen, C_1-C_3alkyl, halogen, hydroxy, C_1-C_3alkoxy, C_1-C_3haloalkoxy, C_1-C_3alkylthio, C_1-C_3alkylsulfinyl, C_1-C_3alkylsulfonyl, amino or cyano;

X_1, X_2, X_3, X_4, X_5, X_6, X_7, X_8, X_9, X_{10}, X_{11}, X_{12}, X_{13}, X_{14}, X_{15}, X_{16}, X_{17}, X_{18}, X_{19}, X_{20}, X_{21}, X_{22}, X_{23}, X_{24} and X_{25} are each independently of the others oxygen or sulfur; and

Y_1 and Y_2 are oxygen or sulfur,

or an agrochemically acceptable salt or tautomer, enantiomer or stereoisomer of such a compound of formula I.

2. A compound of formula I according to claim 1 wherein

R_1 is hydrogen, methyl or halogen;

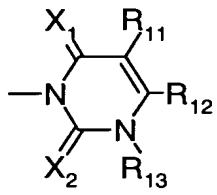
R_2 is hydrogen, C_1-C_{12}alkyl, C_1-C_{12}haloalkyl, C_1-C_{12}alkenyl, C_1-C_{12}alkynyl, C_1-C_{12}haloalkenyl, C_1-C_{12}haloalkynyl, C_1-C_6cycloalkyl-C_1-C_4alkyl, C_1-C_6halocycloalkyl-C_1-C_4alkyl, cyano-C_1-C_{12}alkyl, C_1-C_6alkoxy-C_1-C_4alkyl, C_1-C_4alkoxy-C_1-C_2alkoxy-C_1-C_2alkyl,

di(C_1-C_4alkoxy)C_1-C_2alkyl, C_1-C_6alkylthio-C_1-C_4alkyl, C_1-C_6alkylsulfinyl-C_1-C_4alkyl, C_1-C_6alkylsulfonyl-C_1-C_4alkyl, hydroxy-C_1-C_{12}alkyl, C_1-C_6alkylcarbonyl-C_1-C_4alkyl, C_1-C_6haloalkylcarbonyl-C_1-C_4alkyl, C_1-C_6alkoxycarbonyl-C_1-C_4alkyl, C_1-C_6alkoxycarbonyl-C_1-C_4haloalkyl, C_1-C_6alkoxycarbonyl-benzyl, C_1-C_6alkenyloxycarbonyl-C_1-C_4alkyl, C_1-C_6alkynyloxycarbonyl-C_1-C_4alkyl, C_1-C_6alkylcarbonyloxy-C_1-C_4alkyl, C_1-C_6alkenylcarbonyloxy-C_1-C_4alkyl, C_1-C_6cycloalkylcarbonyloxy-C_1-C_4alkyl, benzoyloxy-C_1-C_4alkyl, C_1-C_6alkoxycarbonyloxy-C_1-C_4alkyl, C_1-C_6alkylaminocarbonyl-C_1-C_4alkyl, C_1-C_6alkylaminocarbonyl-benzyl, or C_1-C_4alkyl substituted by phenyl or by heterocyclyl, wherein the phenyl and heterocyclyl group may be substituted one or more times by halogen, C_1-C_6alkyl, C_1-C_6haloalkyl, C_1-C_6alkenyl, C_1-C_6alkynyl, C_1-C_6haloalkenyl, C_1-C_6haloalkynyl, C_1-C_6cycloalkyl-C_1-C_4alkyl, C_1-C_6halocycloalkyl-C_1-C_4alkyl, cyano-C_1-C_{12}alkyl, C_1-C_6alkoxy-C_1-C_4alkyl, C_1-C_6alkylthio-C_1-C_4alkyl, C_1-C_6alkylsulfinyl-C_1-C_4alkyl, C_1-C_6alkylsulfonyl-C_1-C_4alkyl, hydroxy-C_1-C_{12}alkyl, C_1-C_6alkylcarbonyl-C_1-C_4alkyl, C_1-C_6alkoxycarbonyl-C_1-C_4alkyl, C_1-C_6alkoxycarbonyl-C_1-C_4haloalkyl, C_1-C_6alkylcarbonyloxy-C_1-C_4alkyl, C_1-C_6alkoxycarbonyloxy-C_1-C_4alkyl, C_1-C_4alkoxy-C_1-C_2alkoxy-C_1-C_2alkyl or by phenyl;

R_3 is hydrogen, C_1-C_{12}alkyl, C_1-C_{12}haloalkyl or unsubstituted or substituted phenyl;

R_4 is hydrogen or C_1-C_6alkyl;

W is a group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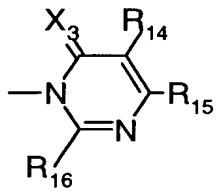
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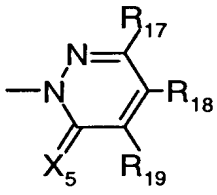
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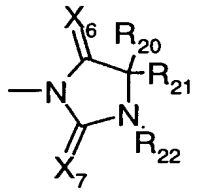
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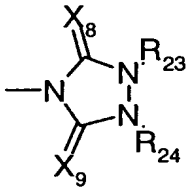
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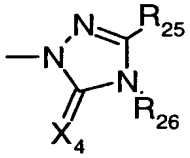
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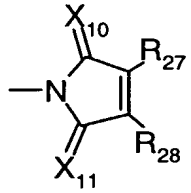
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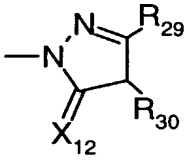
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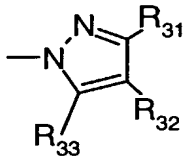
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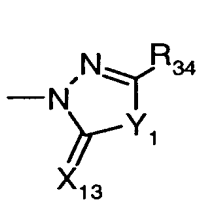
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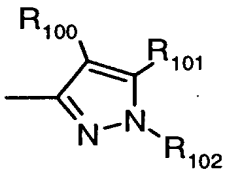
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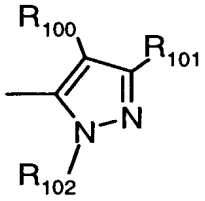
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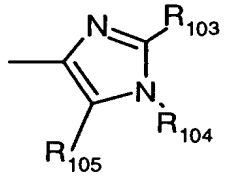
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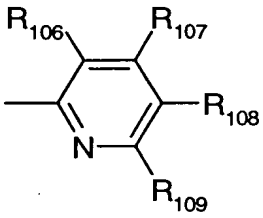
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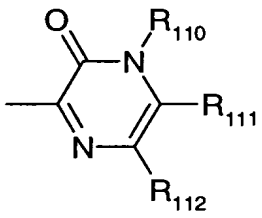
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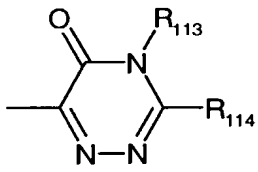
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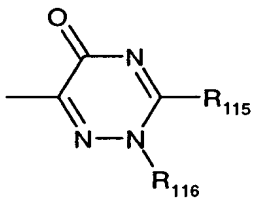
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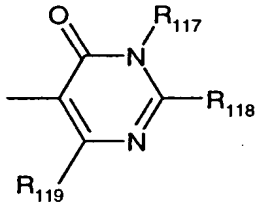
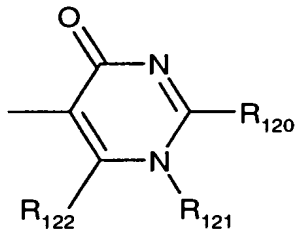

(W107) or


(W108) ;

R_{11} is hydrogen, C_1-C_3alkyl, halogen, C_1-C_3haloalkyl or cyano;

R_{12} is C_1-C_3alkyl, C_1-C_3haloalkyl, C_1-C_3alkyl-S(O)$_{n1}$-, C_1-C_3haloalkyl-S(O)$_{n1}$- or cyano; and

R_{13} is C_1-C_3alkyl, C_1-C_3haloalkyl or amino; or

R_{12} and R_{11} or R_{12} and R_{13} together form a C_3- or C_4-alkylene bridge which may be substituted by halogen, C_1-C_3haloalkyl or by cyano;

R_{14} is hydrogen, C_1-C_3alkyl, halogen, C_1-C_3haloalkyl or cyano; and

R_{15} is C_1-C_3alkyl, C_1-C_3haloalkyl, C_1-C_3alkyl-S(O)$_{n2}$-, C_1-C_3haloalkyl-S(O)$_{n2}$- or cyano; or

R_{15} and R_{14} together form a C_3- or C_4-alkylene bridge which may be substituted by halogen, C_1-C_3haloalkyl or by cyano;

R_{16} is hydrogen, C_1-C_3alkyl, halogen, C_1-C_3haloalkyl, C_1-C_3alkoxy, C_1-C_3haloalkoxy, C_1-C_3alkylthio, C_1-C_3alkylsulfinyl, C_1-C_3alkylsulfonyl or cyano;

n_1 and n_2 are 0, 1 or 2;

R_{17} is hydrogen, C_1-C_3alkyl, halogen or cyano; and

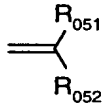
R_{18} is C_1-C_3alkyl, halogen, C_1-C_3haloalkyl, C_1-C_3alkylthio, C_1-C_3alkylsulfinyl, C_1-C_3alkylsulfonyl or cyano; or

R_{18} and R_{17} together form a C_3- or C_4-alkylene or C_3- or C_4-alkenylene bridge, both of which may be substituted by halogen, C_1-C_3alkyl or by C_1-C_3haloalkyl;

R_{19} is hydrogen, halogen, C_1-C_3alkyl or amino; or

R_{19} and R_{18} together form a C_3- or C_4alkylene or C_3- or C_4-alkenylene bridge, both of which may be substituted by halogen, C_1-C_3alkyl or C_1-C_3haloalkyl;

R_{20} and R_{21} are each independently of the other hydrogen or C_1-C_4alkyl; or

R_{20} and R_{21} together are a group  ;

R_{051} and R_{052} are each independently of the other C_1-C_4alkyl; or

R_{051} and R_{052} together form a C_4- or C_5-alkylene bridge;

R_{051} and R_{22} together form a C_3alkylene bridge;

R_{22} is hydrogen or C_1-C_3alkyl; or

R_{22} and R_{20} or R_{22} and R_{21} together form a C_3-C_5alkylene bridge which may be interrupted by oxygen or by –C(O)- and/or substituted by halogen, C_1-C_4alkyl, C_1-C_3haloalkyl, C_2-C_4alkenyl, C_1-C_3alkoxycarbonyl, C_1-C_3alkylcarbonyloxy, C_1-C_3alkylsulfonyloxy or by hydroxy;

R_{23} is hydrogen, C_1-C_3alkyl or C_1-C_3haloalkyl; or

R_{23} and R_{24} together form a C_3-C_5alkylene bridge which may be interrupted by oxygen, sulfur, -S(O)-, -$S(O)_2$- or by -C(O)-;

R_{25} is hydrogen, halogen, C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4alkoxy, C_1-C_4haloalkoxy, C_1-C_4alkylthio, C_1-C_4haloalkylthio, C_1-C_4alkylsulfinyl, C_1-C_4haloalkylsulfinyl, C_1-C_4alkylsulfonyl, C_1-C_4haloalkylsulfonyl or cyano; and

R_{26} is hydrogen, C_1-C_4alkyl or C_1-C_4haloalkyl; or

R_{26} and R_{25} together form a C_3-C_5alkylene bridge which may be interrupted by oxygen or by -C(O)- and/or substituted by halogen, C_1-C_4alkyl, C_1-C_3haloalkyl, C_2-C_4alkenyl, C_1-C_3alkoxy-carbonyl, C_1-C_3alkylcarbonyloxy, C_1-C_3alkylsulfonyloxy or by hydroxy;

R_{27} and R_{28} are each independently of the other hydrogen or C_1-C_4alkyl; or

R_{27} and R_{28} together form a C_3-C_5alkylene bridge or a C_4alkenylene bridge which may be interrupted by oxygen, sulfur, -S(O)-, -$S(O)_2$- or by -C(O)-;

R_{29} and R_{30} are each independently of the other hydrogen or C_1-C_4alkyl; or

R_{29} and R_{30} together form a C_3-C_5alkylene bridge which may be interrupted by oxygen, sulfur, -S(O)-, -$S(O)_2$- or by -C(O)-;

R_{31} is hydrogen, C_1-C_4alkyl or C_1-C_4haloalkyl; and

R_{32} is hydrogen, C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4alkylthio, C_1-C_4alkylsulfinyl, C_1-C_4alkylsulfonyl, cyano or nitro; or

R_{31} and R_{32} together form a C_3-C_5alkylene bridge which may be interrupted by oxygen, sulfur, -S(O)-, -$S(O)_2$- or by -C(O)-;

R_{33} is hydrogen, C_1-C_3alkyl, halogen, C_1-C_3haloalkyl, C_1-C_3alkoxy, C_1-C_3haloalkoxy, C_1-C_3alkylthio, C_1-C_3alkylsulfinyl, C_1-C_3alkylsulfonyl, amino, C_1-C_3alkylamino, C_1-C_3alkylcarbonylamino, C_1-C_3haloalkylcarbonylamino or cyano;

R_{34} is C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4alkoxy or C_1-C_4alkylthio;

R_{100} is hydrogen, halogen, nitro, amino, cyano, C_1-C_3alkyl, C_2- or C_3-alkenyl or C_2- or C_3-alkynyl;

R_{101} is hydrogen, halogen, nitro, amino, cyano, hydroxy, mercapto, C_1-C_3alkyl, C_1-C_3haloalkyl, C_2- or C_3-alkenyl, C_2- or C_3-alkynyl, C_1-C_3alkoxy, C_1-C_3haloalkoxy, C_1-C_3alkylthio, C_1-C_3alkylsulfinyl, C_1-C_3alkylsulfonyl, C_1-C_3haloalkylthio, C_1-C_3haloalkylsulfinyl, C_1-C_3haloalkylsulfonyl, $FS(O)_2$-, $ClS(O)_2$-, C_1-C_6alkylsulfonyloxy, C_1-C_6haloalkylsulfonyloxy, C_1-C_3alkylcarbonyl, HC(O)-, HOC(O)-, ClC(O)-, FC(O)-, C_1-C_3alkoxycarbonyl, $H_2NC(O)$- or $H_2NC(S)$-;

R_{102} is hydrogen, C_1-C_6alkyl, C_3-C_6alkenyl, C_3-C_6alkynyl, C_3-C_6cycloalkyl, C_1-C_6haloalkyl, C_1-C_3alkylsulfonyl, or C_1-C_6alkyl which may be substituted by cyano, HO-, HOC(O)-, C_1-C_3-alkoxycarbonyl or by HC(O)-; or,

when W is a group W_{100},

R_{102} and R_{101} together form a C_3-C_5alkylene bridge which may be interrupted by oxygen, sulfur, -S(O)-, -$S(O)_2$- or by -C(O)- and/or substituted by hydroxy or by halogen;

R_{103} is as defined for R_{101};

R_{104} is as defined for R_{102};

R_{105} is as defined for R_{100};

R_{106} is hydrogen, halogen, amino, nitro, hydroxy, C_1-C_3alkyl or C_1-C_3alkoxy;

R_{107} is hydrogen, halogen, amino, hydroxy, C_1-C_3alkyl, C_1-C_3haloalkyl, HC(O)-, HOC(O)-, hydroxy-C_1-C_3alkyl, C_1-C_3alkoxy or C_1-C_3haloalkoxy; and

R_{108} is hydrogen, halogen, nitro, amino, cyano, HC(O)-, HOC(O)-, $H_2NC(O)$-, $H_2NC(S)$-, hydroxy, HS-, C_1-C_3alkyl, C_1-C_3haloalkyl, C_2- or C_3-alkenyl, C_1-C_3alkoxy, C_1-C_3haloalkoxy, C_1-C_3alkylcarbonyl, C_1-C_3alkoxycarbonyl, C_1-C_3alkylthio, C_1-C_3haloalkylthio, C_1-C_3alkylsulfinyl, C_1-C_3haloalkylsulfinyl, C_1-C_3alkylsulfonyl, C_1-C_3haloalkylsulfonyl, C_1-C_3alkylsulfonyloxy or C_1-C_3haloalkylsulfonyloxy;

R_{109} is as defined for R_{107};

R_{107} and R_{108} together form a C_3-C_5alkylene bridge which may be interrupted by oxygen, sulfur, -S(O)-, -$S(O)_2$- or by -C(O)- and/or substituted by hydroxy or by halogen;

R_{108} and R_{109} together form a C_3-C_5alkylene bridge which may be interrupted by oxygen, sulfur, -S(O)-, -$S(O)_2$- or by -C(O)- and/or substituted by hydroxy or by halogen;

R_{110} is hydrogen, C_1-C_3alkyl, C_1-C_3haloalkyl, C_3-C_4alkenyl or C_3-C_4alkynyl;

R_{111} is as defined for R_{108};

R_{112} is as defined for R_{109};

R_{111} and R_{112} together form a C_3-C_5alkylene bridge which may be interrupted by oxygen, sulfur, -S(O)-, -$S(O)_2$- or by -C(O)- and/or substituted by hydroxy or by halogen;

R_{110} and R_{111} together form a C_3-C_5alkylene bridge which may be interrupted by oxygen, sulfur, -S(O)-, -$S(O)_2$- or by -C(O)- and/or substituted by hydroxy or by halogen, wherein a CH_2 group is bonded to the N atom of the pyrazinone;

R_{113} is as defined for R_{110};

R_{114} is as defined for R_{108};

R_{113} and R_{114} together form a C_3-C_5alkylene bridge which may be interrupted by oxygen, sulfur, -S(O)-, -$S(O)_2$- or by -C(O)- and/or substituted by hydroxy or by halogen, wherein a CH_2 group is bonded to the N atom of the triazinone;

R_{115} is as defined for R_{108};

R_{116} is as defined for R_{110};

R_{115} and R_{116} together form a C_3-C_5alkylene bridge which may be interrupted by oxygen, sulfur, -S(O)-, -$S(O)_2$- or by -C(O)- and/or substituted by hydroxy or by halogen, wherein a CH_2 group is bonded to the N atom of the triazinone;

R_{117} is as defined for R_{110};

R_{118} is as defined for R_{108};

R_{119} is as defined for R_{106};

R_{117} and R_{118} together form a C_3-C_5alkylene bridge which may be interrupted by oxygen, sulfur, -S(O)-, -$S(O)_2$- or by -C(O)- and/or substituted by hydroxy or by halogen, wherein a CH_2 group is bonded to the N atom of the pyrimidinone;

R_{120} is as defined for R_{108};

R_{121} is as defined for R_{110};

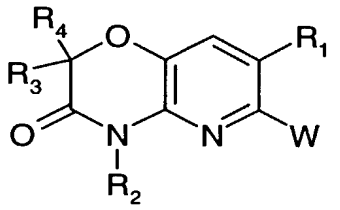
R_{122} is as defined for R_{106};

R_{121} and R_{120} together form a C_3-C_5alkylene bridge which may be interrupted by oxygen, sulfur, -S(O)-, -$S(O)_2$- or by -C(O)- and/or substituted by hydroxy or by halogen, wherein a CH_2 group is bonded to the N atom of the pyrimidinone;

X_1, X_2, X_3, X_4, X_5, X_6, X_7, X_8, X_9, X_{10}, X_{11}, X_{12} and X_{13} are each independently of the others oxygen or sulfur; and

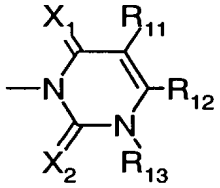
Y_1 is oxygen or sulfur.

3. A process for the preparation of compounds of formula I according to claim 1, which process comprises, for the preparation of compounds of formula I



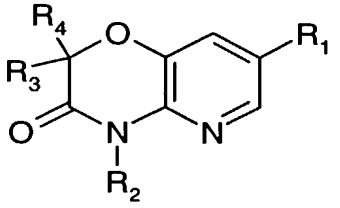
(I)

wherein R_1, R_2, R_3 and R_4 are as defined in claim 1 and W is a group W_1



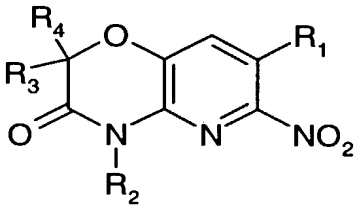
(W_1),

wherein R_{11}, R_{12}, R_{13}, X_1 and X_2 are as defined in claim 1, converting a compound of formula XXX



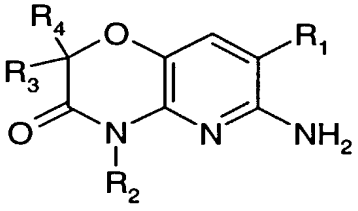
(XXX),

wherein R_1, R_2, R_3 and R_4 are as defined, by means of aromatic nitration, into the compound of formula IIn



(IIn)

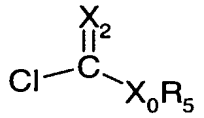
and subjecting that compound to reduction to yield the compound of formula IIa



(IIa),

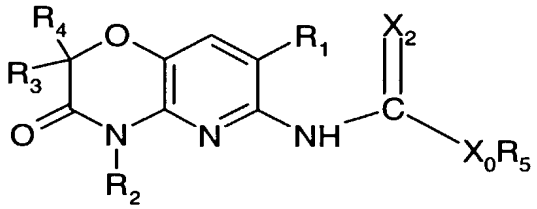
which is either

a) reacted with a compound of formula VI



(VI),

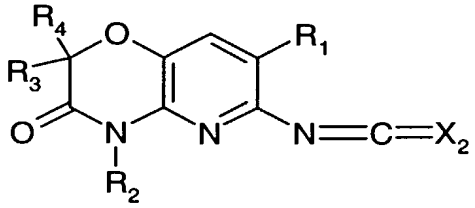
wherein X_2 is as defined in claim 1, X_0 is oxygen, sulfur or amino and R_5 is C_1-Calkyl, to form the compound of formula IIc



(IIc),

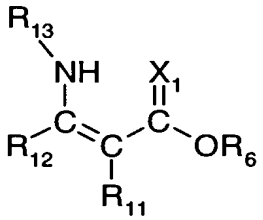
wherein R_1, R_2, R_3, R_4, R_5, X_0 and X_2 are as defined, or

b) treated with phosgene (X_2=O) or thiophosgene (X_2=S) of formula $C(X_2)Cl_2$ or oxalyl chloride, to obtain the compound of formula IId



(IId),

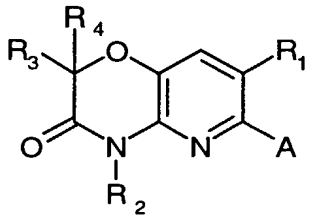
wherein R_1, R_2, R_3, R_4 and X_2 are as defined, and condensing and cyclising the compounds of formulae IIc and IId thereby obtained with an enamine of formula VII



(VII),

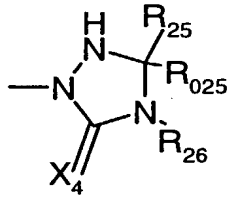
wherein R_{11}, R_{12}, R_{13} and X_1 are as defined and R_6 is C_1-C_4alkyl, in an inert solvent in the presence of from 0.01 to 1.5 equivalents of a suitable base, and then, optionally, further functionalising the substituents X_1, X_2, R_1, R_2, R_{11} and R_{13} according to their definitions.

4. A compound of formula II



(II),

wherein R_1 to R_4 are as defined for formula I and A is fluorine, C_1-C_4alkylthio, C_1-C_4alkylsulfonyl, phenylthio, phenylsulfonyl, C_1-C_4alkylsulfonyloxy, trifluoromethylsulfonyloxy, hydroxy, nitro, amino, isocyanato, isothiocyanato, hydrazino, a group $NHC(X_2)X_0R_5$, $NHC(X_7)X_0R_5$, $NHC(X_8)X_0R_5$, $NHC(X_9)X_0R_5$, $NHC(X_3)R_{16}$, $NHN=C(R_{17})C(O)R_{18}$, $NHC(X_7)N(R_{22})C(R_{20})R_{21}C(X_6)OR_9$, $NHC(X_9)NR_{24}NR_{23}C(X_8)OR_{10}$, $NHC(X_8)NR_{23}NHR_{24}$, $NHN=C(R_{25})COOH$, $NHN=C(R_{25})R_{025}$, $N(C(X_4)\text{-}NHR_{26})N=CR_{25}R_{025}$, $N(C(X_4)NHR_{26})NH_2$, $NHN=C(R_{25})N(R_{26})C(X_4)OR_{84}$, $N(C(X_4)NHR_{26})NHC(O)OR_{84}$, $N(C(X_{19})NHR_{50})NHC(O)OR_{84}$, $NHC(X_{12})NHR_{26}$, $NHC(O)C(R_{28})=C(R_{27})C(O)OR_{85}$, $NHC(=NR_{39})NHR_{38}$, $NHC(Y_2)NR_{40}NHR_{41}$, $NHC(Y_2)NR_{40}NR_{41}C(O)OR_9$, $NHN=C(R_{42})C(O)NHR_{43}$, $NHN=C(R_{42})C(O)N(R_{43})C(O)OR_{85}$, $N(R_{43})COOR_{85}$, $NHC(R_{53})=NNHC(X_{21})OR_{86}$, $NHC(S)NHC(=NR_{57})R_{56}$, $NHC(X_{23})NHR_{58}C(X_{25})NHR_{59}$, $N(C(X_{24})NHR_{59})C(X_{23})X_0R_5$, ethyl, vinyl, ethynyl, $C\equiv CC(O)OR_{86}$, $C\equiv CC(O)R_{87}$, acyl, formyl, cyano, carboxy, $C(O)OR_{89}$, $C(O)C(O)OR_{90}$, $C(O)CH_2COOR_{91}$, $C(O)CH_2C(O)R_{88}$, cyanomethyl, $B(OH)_2$ or



, wherein

R_{16}, R_{17}, R_{18}, R_{20}, R_{21}, R_{22}, R_{23}, R_{24}, R_{25}, R_{26}, R_{27}, R_{28}, R_{38}, R_{39}, R_{40}, R_{41}, R_{42}, R_{43}, R_{50}, R_{53}, R_{56} and R_{57} are as defined in claim 1; R_5, R_9, R_{025}, R_{84}, R_{86}, R_{89}, R_{90} and R_{91} are each independently of the others C_1-C_4alkyl or phenyl; R_{10} and R_{85} are hydrogen or C_1-C_4alkyl; R_{87} and R_{88} are C_1-C_4alkyl, formyl, $CH(C_1$-C_4alkoxy) or C_1-C_4haloalkyl; X_1, X_2, X_3, X_4, X_6, X_7, X_8, X_9, X_{12}, X_{19}, X_{21} and Y_2 are oxygen or sulfur; and X_0 is oxygen, sulfur or amino.

5. A herbicidal and plant-growth-inhibiting composition, comprising a herbicidally effective amount of a compound of formula I on an inert carrier.

6. A herbicidal and plant-growth-inhibiting composition according to claim 5, comprising at least one further co-herbicide as additional component.

7. A method of controlling undesired plant growth, which method comprises applying a compound of formula I, or a composition comprising such a compound, in a herbicidally effective amount to plants or to the locus thereof.

8. Use of a composition according to claim 5 in the control of undesired plant growth.